



*Lectures*  
*on*  
*Theoretical and Physical*  
*Chemistry*

BY  
DR. J. H. VAN 'T HOFF  
PROFESSOR AT THE UNIVERSITY OF BERLIN

TRANSLATED BY  
DR. R. A. LEHFELDT  
PROFESSOR AT THE EAST LONDON TECHNICAL COLLEGE

PART I  
*CHEMICAL DYNAMICS*

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## PREFACE

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THE following work reproduces the lectures given by me at the University of Berlin, under the title of 'Selected Chapters in Physical Chemistry.' It really includes somewhat more, for in the strictly limited time it was only possible to pick out certain leading points, in order to cover the whole subject, in one-hour lectures, through the course of four semesters. So this little book may perhaps be a welcome guide to those who wish to possess themselves of the latest acquisitions of physical chemistry.

J. H. VAN 'T HOFF.

CHARLOTTENBURG,  
*January, 1898.*





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## THE DIVISION OF THE WORK AND THE TREATMENT CHOSEN

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IN the inevitably arbitrary division of any subject it is well to choose so that it may easily be seen where each part belongs. For this reason the treatment adopted by Lothar Meyer in the later editions of his *Modern Theories of Chemistry* seemed to me appropriate for my lectures: in it the whole is divided into Statics and Dynamics. Statics then deals with single substances, i.e. with views on the structure of matter, the conception of atoms and molecules, and on constitution so far as the determining of molecular configuration. Dynamics is devoted to the mutual actions of several substances, i. e. to chemical change, affinity, velocity of reaction, and chemical equilibrium.

To these I have added a third section, in which the chief object is the comparison of one substance with another, and consequently the relations between properties—both chemical and physical—and composition.

In preparing for the press I have preserved this arrangement, only making a change in the order in accordance with the development of chemical science in the last ten years. Until then Dynamics, that is the study of reactions and of equilibrium, took a secondary place. But lately, and especially since the study of chemical equilibrium has been related to thermo-dynamics, and so has steadily gained a broader and safer foundation, it has come into the foreground of the chemical system, and seems more and more to belong there.

The following arrangement is therefore chosen as an experiment:—

First Part: Chemical Dynamics.

Second Part: Chemical Statics.

Third Part: Relations between Properties and Constitution.

The logical advantage gained in this way is essentially that in the First Part it is possible to proceed without any hypothesis on the nature of matter, only the molecular conception being made use of. Not till the Second Part does the atomic hypothesis come to the front, and with it problems of configuration. Finally comes the still very obscure problem of the relation of one body to another.

There are two points, however, that should be referred to. From the logical side it may be objected that Statics is concerned with the simpler problem, since it deals with single substances at rest, whereas Dynamics deals with a complex of substances in action. This objection, however, has less force when one remembers that the single substance corresponds to the state of equilibrium following a completed reaction and indeed the simplest form of equilibrium and accordingly Part II is devoted to the more detailed study of this final state.

From the pedagogic point of view, placing Dynamics first can be dubious only to those chemists who are not well prepared in Physics, and consequently have not mastery over the chief lines of their own subject.

The treatment chosen corresponds with that I have followed in teaching. It consists essentially in developing each generalization from a specially chosen concrete experimental case. On this follow an exhibition—as far as possible graphic—of the leading results, the conclusions drawn, and, lastly, theoretical remarks on the generality and applicability of the conclusions. In accordance with the object mentioned in the preface the special cases chosen are, as far as possible, those that have been dealt with experimentally in my own laboratory.

# PART I

## CHEMICAL DYNAMICS

---

*Contents and arrangement.* Although chemical dynamics is concerned—as the name indicates—essentially with the problem of chemical change, yet in dealing with it the result of chemical change, i.e. chemical equilibrium, occupies the most prominent place. This mode of treatment is in accordance with the plan of the work as described in the introduction: for it was there pointed out that chemical dynamics should be placed first because the theory of chemical equilibrium and its connexion with thermo-dynamics afford a solidier foundation for chemistry.

If then the theory of chemical equilibrium come first, the second section will deal with the process by which that condition is arrived at, i.e. chemical reaction. A new factor—time—has then to be taken into account, and the chief results are the laws of velocity of reaction, in immediate connexion with those of equilibrium. Naturally, then, we have these chapters:—

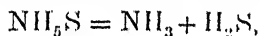
- I. Chemical equilibrium.
- II. Velocity of reaction.



## I. CHEMICAL EQUILIBRIUM

LIKE all natural phenomena, that of chemical equilibrium may be looked at from two essentially different points of view: the two, which are complementary to one another, may be described as the thermo-dynamic and the molecular, or atomistic.

On the one hand, the phenomenon of chemical equilibrium may be looked at purely from the outside, without considering any mechanism on which it depends. Consider, for instance, the decomposition of ammonium sulphide:



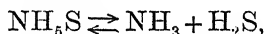
which, as is known, ceases when---both solid compound and gaseous products of decomposition being present---the pressure of the latter reaches a certain maximum value: in this decomposition one sees, from the first point of view, the simple formation, up to a certain limit, of a vapour from a solid of the same composition. Pressure, volume, temperature, state of aggregation, and empirical composition, are then the purely experimental factors with which one is contented. The relation to the physical phenomenon of evaporation is then obvious, and the fundamental laws of thermo-dynamics, applicable to both cases, supply the connecting link.

The matter may be followed out further by taking into account the working mechanism, and this is especially of importance in the case of chemical equilibrium. The state of rest which characterizes an evaporating liquid, when the maximum pressure is reached, is only apparent, depending on simultaneous and equal evaporation and con-

densation; and in the case of ammonium sulphide, this consideration is even more pertinent, since the formation of vapour depends on a decomposition into sulphuretted hydrogen and ammonia. This view attains practical importance when the influence of an addition of ammonia, say, on the equilibrium condition, is to be determined. So the second problem may be described as a more exact knowledge of homogeneous mixtures, and of the phenomena of equilibrium that occur in them.

There is an unmistakable tendency at present to develop the first, pure thermo-dynamic treatment, at the expense of the second, or molecular: a tendency which is justified by the hypothetical character of the latter. But the latter remains, meanwhile, valid, and we will express chemical equilibrium, from this point of view, by a symbol which represents, pictorially, what is to be conceived of the mechanism.

The equilibrium of ammonium sulphide may then be set forth in the following way:



where the opposing arrows represent the two imagined opposing processes, while the formulae give an insight into the composition of the gaseous mixture.

## § 1. CHEMICAL EQUILIBRIUM VIEWED IN ITS EXTERNAL ASPECTS. CONNEXION WITH PHYSICS. APPLICATION OF THERMO-DYNAMICS.

### A. Physical Equilibrium of a Single Substance.

In order to bring out the phenomena of equilibrium in their simplest form, let us follow the changes of which a definite substance is capable, which can only change physically, that is only in regard to its state of aggregation. We can obtain a picture of the phenomena we are considering from the observations of Ramsay<sup>1</sup> and

<sup>1</sup> *Phil. Mag.* 23. 61.

Fischer<sup>1</sup> on evaporation. The details of the method, being chiefly of pure physical interest, need only be briefly referred to; the observations were on the maximal vapour pressure of benzene; they were carried out by Ramsay by the so-called dynamic method—i.e. by determining the boiling point under constant pressure: by Fischer by the so-called static method—i.e. by observations of pressure at known temperatures. The results are given in millimetres of mercury:—

<i>Temperature.</i>	<i>Pressure</i> (Fischer).	<i>Pressure</i> (Ramsay).
0°	26.4	26.54
1	27.87	28.04
2	29.43	29.61
3	31.1	31.26
4	32.84	32.99
5	34.68	34.8
6	36.6	36.69

The two series practically agree, in accordance with the law that ebullition occurs when the maximal pressure equals the pressure of the surroundings.

Let us take next the results for each ten degrees, in order to bring out the leading characteristics of the pressure curve:—

<i>Temperature.</i>	<i>Pressure.</i>	<i>Difference</i> <i>for 10°.</i>	<i>Quotient</i> <i>for 10°</i> <i>difference.</i>
10	45.19	28.94	1.64
20	74.13	43.32	1.58
30	117.45	62.75	1.53
40	180.2	88.1	1.49
50	268.3	120.21	1.45
60	388.51	159.65	1.41
70	548.16	206.84	1.38
80	755.		

It appears that the difference of pressure for 10° difference of temperature rapidly increases, but that the quotient does not alter so noticeably, and only gradually falls a little. We may lay stress on this peculiarity, because it occurs again—for reasons easily understood—in the phenomena of chemical equilibrium, as regards velocity of

reaction. The curve which shows the relation between the pressure  $P$  as ordinate and the temperature  $T$  as abscissa has the well-known form of the line  $AB$  in Fig. 1; the area of the diagram, which includes all possibilities of pressure and temperature, is divided by this line  $AB$  into two parts, of which the lower corresponds to the states in which benzene occurs as (unsaturated) vapour, and the upper to those of (more or less compressed) liquid, while only the boundary line represents the presence of both states.

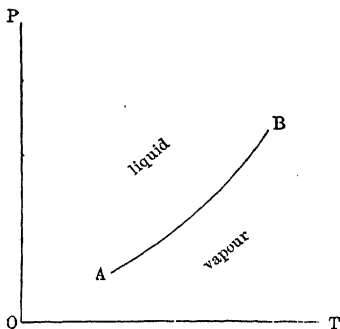


FIG. 1.

Let us introduce now solid benzene with the recent very exact results of Ferche<sup>1</sup>, and set side by side these results, and those (also determined by Ferche) for the liquid at the same temperatures, the liquid being in this case undercooled:—

Temperature.	Pressure (liquid).	Pressure (solid).
0°	26.6	24.61
1	28.1	26.31
2	29.65	28.17
3	31.3	30.18
4	33.06	32.34
5	34.93	34.64
5.58	39.06	36.06

Representing these graphically by Fig. 2, the two leading conclusions stand out clearly:—

1. At the melting point  $D$  (near  $5.58^\circ$ )<sup>2</sup> the pressures of the solid and liquid become equal.

2. Below the melting point the solid has the lower pressure,  $CD$ ; above it would have the higher pressure, if it were capable of existence.

<sup>1</sup> *Inaugural dissertation*, Halle, 1890.

<sup>2</sup> Direct observation gave  $5.455^\circ$ .

The melting point thus appears as the point of intersection of the two pressure curves<sup>1</sup>.

Both results are clearly general. Imagine solid and liquid benzene, separate, but side by side in vacuum, then a process of distillation would cause a conversion into the form possessing the lower pressure; consequently when the pressures were equal (near  $5.58^{\circ}$  in this case) no change—in other words, equilibrium—would occur, which is the condition for the melting point. Below the melting point, where

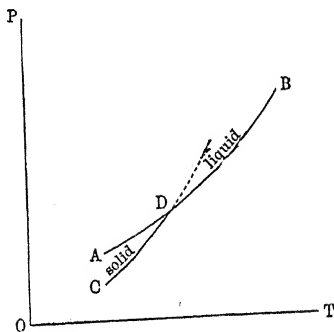


Fig. 2.

the pressure of the solid is the lower, distillation from liquid to solid, i.e. solidification, occurs, while above the melting point the reverse is to be expected.

Consider finally the curves of Fig. 2 with reference to the stability of the conditions represented. AB, the curve corresponding to liquid in contact with saturated vapour, is cut by CD into two parts; the DB corresponds to liquid benzene above the melting point, and therefore is a stable condition; the lower AD, on the contrary, is liquid below the melting point, in the undercooled condition which solidifies on contact with the smallest quantity of solid benzene, or on stirring, and may therefore be described as unstable. The line CD, corresponding to the solid state, may also be produced, and then to the right of D would represent solid above the melting point, a condition not only unstable, but unrealizable, as for instance ice above  $0^{\circ}$ .

As in the following pages we shall be concerned chiefly with stable states, we will bring together in Fig. 3 only

<sup>1</sup> It may be remarked, in passing, that the above result might be obtained even more accurately by means of the Bremer-Frowein differential pressure gauge (*Zeits. f. Phys. Chem.* i. 5).

the branches CD and DB of the curves. The field of the diagram is then, again, divided into an upper and lower part, of which the latter, lying under CDB, refers, as before (Fig. 1), to (unsaturated) vapour; the upper refers now not only to the liquid, but also to the solid state, and we are concerned to find the boundary between the two. This obviously starts from D, and its continuation corresponds to a series of melting points under increasing pressure, also determined by Ferche. The highest pressure used in

the experiments was 3742.7 mm., and was accompanied by a rise of only  $0.143^\circ$  in the melting point. The boundary line between solid and liquid is accordingly nearly vertical, inclining slightly to the right, as shown by DE in Fig. 4.

Consideration of the effect of pressure on the melting point leads now to a more exact definition of the point D. Hitherto it has been described simply as the melting point; but D really represents only the melting point under a definite pressure, viz. that of the maximum vapour pressure. The customary melting point, observed under atmospheric

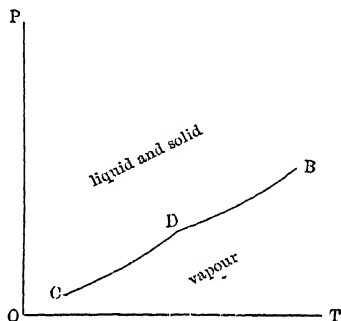


FIG. 3.

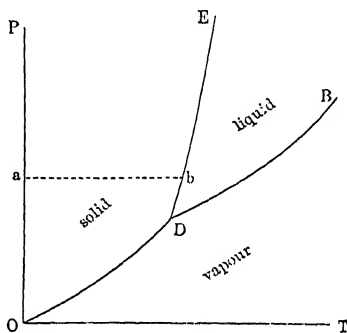


FIG. 4.

pressure, is shown by the point *b*, which can be obtained by a simple construction; *oa* is measured along the vertical axis to represent the atmospheric pressure, and from *a* the horizontal line *ab* drawn. Practically the

difference is unnoticeable, being only  $0.03^{\circ}$  in the case chosen—that of benzene—so that  $\nu$  only lies that much lower than the melting point usually observed. But theoretically there is an important fact to notice.  $\nu$  is the only point at whose temperature the three conditions, solid, liquid, and vapour, can exist together;  $\nu$  is accordingly called the triple point.

The treatment becomes more intelligible by noting that the figure consists of—first, areas; second, lines which bound these areas; and, thirdly, a point in which the lines meet. The areas refer to circumstances in which the benzene is present only in one state, whether solid, liquid, or vaporous; the lines to those in which two states are possible, combinations of solid and liquid, or solid and vapour, or liquid and vapour; while, finally, under the circumstances indicated by the point of intersection all three, solid, liquid, and vapour, can exist side by side.

If we complete the diagram by prolonging the curve  $\nu$  as far as possible, one result is at once seen: the boundary between liquid and vapour vanishes at the critical point—for benzene at a temperature of  $280.6^{\circ}$  and pressure of 49.5 atmospheres; the boundary line going from  $\nu$  to the right towards  $\beta$  consequently stops there, and the liquid area and vapour area become continuous. The line from  $\nu$  to the left, representing maximum vapour pressure of the solid substance, may be continued by help of the empirical observation that equal differences of temperature correspond to equal ratios of pressure; accordingly the pressure never falls to zero, but approaches it so nearly that if the origin  $o$  be made to stand for the absolute zero of temperature, we may safely take  $o$  as the starting-point of the vapour pressure curve<sup>1</sup>. There remains the rising curve  $\nu\epsilon$ , the boundary between solid and liquid, to follow out; its end point has not been reached, but it is possible—it may even be regarded as probable—that, at some tempera-

<sup>1</sup> It will be shown later that there are theoretical grounds for assuming the pressure to be zero when the absolute temperature is zero.

ture and pressure, solid and liquid too lose their sharp distinction, and lead into an amorphous half-liquid, half-solid state. In the diagram the end point E may represent that, and we may add that Spring appears to have passed this point, for powder of solid metals exposed by him to a pressure of more than 1,000 atmospheres gave, by its homogeneity, crystalline structure, &c., quite the impression of having been melted (Lehmann's flowing crystals).

If these facts and their graphical representation are treated from the thermo-dynamical side, the well-known

reversible cyclic process applied to evaporation is available.

Let 1 kilogram of benzene be evaporated at  $T$  under constant (saturation) pressure; the corresponding increase of volume,  $V$  cub. metres, is shown by AB in Fig. 5. Let the vapour cool by  $dT$  without gain or loss of heat, the pressure and volume being shown by BC; the two processes in the

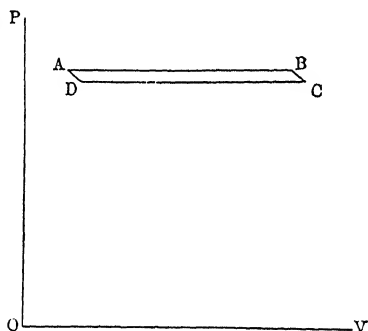


FIG. 5.

opposite sense CD and DA complete the cycle, ABCD being the work given out  $= \int V dP$  kilogrammetres if the pressure be given in kilograms per sq. metre; this work in calories is  $A \int V dP$  ( $A = \frac{1}{423}$ ). According to the second law of thermo-dynamics, this is equal to the quantity of heat  $q$  applied for the evaporation at  $T$ , multiplied by the quotient of the fall of temperature  $dT$  by the temperature  $T$ ; that is,

$$A \int V dP = q \frac{dT}{T}.$$

This is the strict thermo-dynamic expression. It regulates equally the three curves relating respectively to the evaporation of the liquid, of the solid, and to the fusion;  $q$  is according to circumstances the latent heat of evaporation



of the liquid, of the solid, or the latent heat of fusion;  $V$  is the increase of volume accompanying the evaporation of the liquid or the solid, or finally the fusion of the solid.

Let us apply this, next, to the evaporation of liquid benzene, for which a pressure 34.93 mm. of mercury was found at  $5^\circ$ , 36.06 mm. at  $5.58^\circ$ , consequently an increase of 1.13 for  $0.58^\circ$  or in kilograms per sq. metre  $1.13 \times 13.6 = 15.37$ . The value of  $\frac{dP}{dT}$  is therefore, taking this moderately small change as an infinitesimally small one,  $15.37 \div 0.58 = 26.5$ , and therefore

$$AT \frac{dP}{dT} = \frac{273 + 5.29}{423} \times 26.5 = 17.5.$$

The value of  $\frac{q}{V}$  to be compared with this is derived from the heat of evaporation and the increase of volume of a kilogram. The latent heat at  $5.28$ , according to Regnault, is 108. The increase of volume may be found by calculating the volume of a kilogram of benzene vapour at  $5.28^\circ$  and 35.5 mm., according to the laws of Avogadro, Gay-Lussac, and Boyle, taking the volume of a kilogram of hydrogen at  $0^\circ$  and 760 mm. as (in cub. metres)  $\frac{1}{0.08956}$ ; it is

$$\frac{1}{0.08956} \times \frac{2(1 + 0.00366 \times 5.28)}{78} \times \frac{760}{35.5} = 6.25,$$

2 and 78 respectively being the molecular weights of hydrogen and benzene. From this has to be subtracted the volume of the liquid benzene—a quantity less than 0.002 cub. metres per kilogram, which need only be considered when the highest accuracy is attempted; consequently

$$\frac{q}{V} = \frac{108}{6.25} = 17.3,$$

differing little from the previous value 17.5.

A considerable simplification can be made in the fundamental equation, by introducing once for all the application

of the laws of Avogadro, Gay-Lussac, and Boyle just used, and by neglecting the volume of the liquid. Putting the combination of these laws in the known form

$$APV = 2T,$$

where  $V$  is the volume of a kilogram-molecule, so that the factor of  $T$  is the same for all gases and vapours (it may be calculated for hydrogen from the data: 1 litre at  $0^\circ$  and 760 mm. weighs 0.08956 gm.; therefore  $T = 273$ ,  $P = 10333$ ,  $V = \frac{2}{0.08956}$ , and  $\frac{APV}{T} = 2$  approximately), we have from the fundamental equation

$$q \frac{dT}{T} AV dP = 2T \frac{dP}{P},$$

or 
$$\frac{d \log P}{dT} = \frac{q}{2T^2},$$

wherein  $q$  now refers to the kilogram-molecule.

The former proof may now be put more simply:

$$\frac{dP}{PdT} = \frac{15.37}{35.5 \times 13.6 \times 0.58} = 0.0549,$$

$$\frac{q}{2T^2} = \frac{108 \times 78}{2 \times (278.28)^2} = 0.0544.$$

The new equation, however, gives an insight into the course of the vapour pressure curve. For the integral of it, assuming  $q$  to be constant, which is not far from the truth,

$$\log P = -\frac{q}{2T} + \text{const.},$$

shows that for equal temperature differences—say of  $10^\circ$ —the quotient

$$\log \frac{P_{T+10}}{P_T} = \frac{5q}{T(T+10)},$$

on account of the somewhat high value of the absolute temperature does not change much, and only increases a little with rise of temperature.

It may be remarked in passing that this equation brings

out the probability mentioned on p. 18, that at the absolute zero the pressure vanishes, for

$$\log \frac{P_{10}}{P_0} = \frac{5q}{10 \times 0} = \infty,$$

which can only be the case if  $P_0 = 0$ .

### B. Chemical Equilibrium of a Single Substance.

Consider now a single substance which, without changing its composition, can suffer a chemical change, i.e. into an isomeric or polymeric form. If we take these chemical changes, without first dealing with the physical changes that may possibly occur at the same time, their representation is entirely similar to the former case. A notable example, but one not yet sufficiently investigated, is to be found in the mutual conversion of cyanic acid, cyanuric acid, and cyamelide. Troost and Hautefeuille<sup>1</sup> found that at a given temperature equilibrium exists between cyanuric and cyanic acid, determined by a definite pressure of (gaseous) cyanic acid, corresponding exactly to the equilibrium between water or ice and steam; only here the conversion depends on a chemical change thus,

$\text{H}_2\text{O (liquid)} \rightleftharpoons \text{H}_2\text{O (vapour)}$  or  $\text{water} \rightleftharpoons \text{steam}$ ,  
and on the other hand

cyanuric acid  $\rightleftharpoons$  cyanic acid or  $\text{C}_3\text{N}_3\text{O}_3\text{H}_3 \rightleftharpoons 3\text{CNOH}$ .

A corresponding equilibrium occurs at lower temperatures between cyamelide and cyanic acid, and to complete the analogy with the behaviour of water, ice, and steam it is observed that, according as the temperature is above or below  $150^\circ$ , the cyanic acid condenses to cyanuric acid or to cyamelide. The entire action is thus given by Fig. 6, quite similar to Fig. 5, in which the former areas of steam, ice, and water are replaced respectively by those of cyanic acid, cyamelide, and cyanuric acid.

The direct conversion of cyamelide into cyanuric acid,

<sup>1</sup> *Compt. Rend.* 67. 1345.

which is to be expected above  $150^{\circ}$ , has been observed experimentally; only the reverse process, which should occur below that temperature, is wanting<sup>1</sup>. I do not doubt, however, that with the new dilatometer<sup>2</sup> adapted to small quantities of material, this extremely slow change might be observed.

From the comparison with the physical phenomena of equilibrium and change of state a division of the chemical phenomena may be made, according as they are comparable with evaporation or with fusion. Of the first kind are the early known case of calcium carbonate, and the conversion of cyamelide or cyanuric acid into cyanic acid;

or, briefly, the simplest case is that indicated by the curves OD and DB. Here we are concerned with pressure measurements at constant temperature, as will often be the case in the sequel. The second group, comparable with fusion and solidification, has been studied more recently; in the illustration

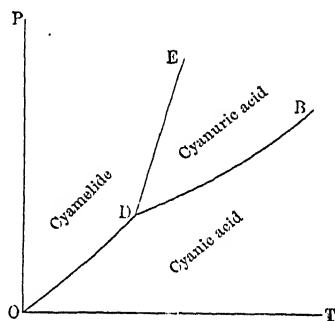


FIG. 6.

chosen it includes the mutual conversion of cyamelide and cyanuric acid; in it we are concerned with measurements of the temperature of conversion under definite pressure, i. e. study of the curve DE.

Considering the subject somewhat more abstractly, it may be noted that in both the physical and chemical cases we have to consider the three curves OD, BD, ED in essentially the same manner to find the temperature and pressure at which two states can exist side by side in equilibrium; consequently in each case, besides the principal experimental method, a second is available, which brings out in practice

<sup>1</sup> Van 't Hoff-Cohen, *Studien zur Chemischen Dynamik*, 1896, p. 178.

<sup>2</sup> *Zeitschr. f. Phys. Chem.* 17. 49.

the expected analogy. In case of equilibrium between liquid and vapour, instead of measuring the pressure at constant temperature (statical method), one may carry out boiling-point determinations under given pressure (dynamical method). On the other hand, in the equilibrium between solid and liquid, instead of observing the temperature under given pressure, one may observe the pressure corresponding to a given temperature, as was done by De Visser<sup>1</sup> with his manocryometer. Thus we have the following summary:—

	<i>Equilibrium between</i>	
	<i>Vapours and solid or liquid.</i>	<i>Solid and liquid (condensed system).</i>
Det. of temp. at given press.	Dynamic method	Customary method
Det. of press. at given temp.	Static method	Manocryometer

Chemical equilibrium comparable with evaporation will be more completely discussed later; we will here consider that similar to solidification and fusion. It has been demonstrated specially by Lehmann<sup>2</sup> in innumerable cases in which a substance can crystallize in more than one form; whether this is to be regarded as a physical or chemical change is largely a matter of definition; but the chief point is that, as with solidification or fusion, there is a temperature limit above and below which one form finally prevails. The phenomena may be described in the case of sulphur, where everything has been made clear, largely through Reicher's<sup>3</sup> researches. It is well known that sulphur exists in rhombic (octahedral) and in monosymmetric (prismatic) form, and it has been found that 95.6° is the temperature limit, below which the rhombic, above which the monosymmetric finally prevails. The peculiarity of the process, as compared with fusion, is the slowness with which change takes place, so that, e.g., rhombic sulphur may keep its form well over 95.6° for a long time. It is best, on that account, to divide the investigation into two

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 9. 767.

<sup>2</sup> *Moleculärphysik*, 1889.

<sup>3</sup> Van 't Hoff-Cohen, *Studien aus...*

stages: first, to observe the mutual conversion, and then to find the exact temperature limit. The first can easily be done with the microscope, using a special objective table (c, Fig. 7) adaptable to any microscope; the table can be heated from the side at A, and is provided with a thermometer at B. The substance is placed on a slide under a thin-walled flat watch-glass as cover, moistened with solvent, and observed under alternate heating and cooling. The conversion is soon

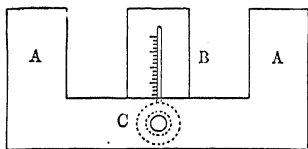


FIG. 7.

observed, and then the preparation can be obtained in a half-converted state, with a clear line of demarcation between the two forms; the displacement of the line in one direction or the other may then be observed with the eye-piece micrometer at temperatures more or less removed from the required limit. The same thing may often be observed microscopically by crystallization from a solvent in the one or the other form according to temperature, provided supersaturation be avoided.

The fact and the approximate temperature being settled so, the exact determination may best be carried out with a dilatometer, the change—frequently considerable—in volume accompanying the conversion serving as criterion. The instrument in its latest form<sup>1</sup>, suited for use with a very small amount of material, consists of a capillary A (Fig. 8), fused on to a reservoir B that can be filled from C. After C is sealed off and the apparatus is pumped out through A, the liquid D, e.g. petroleum, is allowed to enter. If the change is slow, as in the case of sulphur, the liquid may

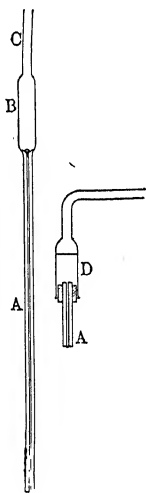


FIG. 8.

be one that dissolves the substance in question slightly (for sulphur a mixture of turpentine and carbon disulphide). After a millimetre scale is attached to A the sensitiveness of the dilatometer may be much increased by causing the conversion to take place several times. It is then carried out about half, and the change studied from degree to degree, the instrument being kept, often for hours, at constant temperature, to see whether continuous expansion (change in one sense), or continuous contraction (change in the other sense), or constancy of volume (equilibrium) occurs.

As example, a few numbers for sulphur may be quoted:—

Temp. 95.1°	Time	5	30	55	65 minutes
	Height of oil column	343.5	340.5	335.7	333 mm.
Temp. 96.1°	Time	5	30	55	60 minutes
	Height of oil column	342.7	354.7	360.5	361.5 mm.

from which it follows that 95.6° is the temperature of conversion.

Going further, and still following the physical analogy of melting and freezing, the question arises: How is the temperature of conversion affected by pressure? The general formula above (p. 19),

$$AVdP = q \frac{dT}{T},$$

again gives the answer, and is confirmed by the experiment, which consists in observing the change of temperature under the influence of an applied (carbon dioxide) pressure. The temperature was found to rise by 0.049° per atmosphere<sup>1</sup>. Now in the above equation

$$T = 273 + 95.6;$$

$V$  is the increase of volume of 1 kilogram of sulphur in passing from the rhombic to the monosymmetric form,

<sup>1</sup> It may be remarked that the experiment would be better done in the way adopted by De Visser—the top of the capillary being sealed off, and the equilibrium pressure of the conversion so obtained of its own accord.





under ordinary pressures the monosymmetric form crystallizes out of molten sulphur, at pressures above 400 atmospheres the rhombic form is obtained direct without undercooling.

Finally, there is for sulphur the peculiarity that it has two melting points, according to its crystalline form:  $120^\circ$  is the well-known melting point of the monosymmetric; while if one succeeds in heating the rhombic form so far without conversion, it shows, according to Brodie<sup>1</sup>, the second melting point,  $114.5^\circ$ . Even this may be explained by the diagram, and calculated, remembering that the second melting point is the temperature at which rhombic and liquid sulphur have the same pressure, i. e. at which OD and GF cut in  $a$ .

Assuming the equation previously given—

$$\log P = B - \frac{q}{2T},$$

let us apply it to rhombic, liquid, and monosymmetric sulphur, calling  $q_r$ ,  $q_g$ , and  $q_m$  the latent heats of evaporation respectively:

$$\log P_r = B_r - \frac{q_r}{2T}, \quad \log P_g = B_g - \frac{q_g}{2T},$$

$$\log P_m = B_m - \frac{q_m}{2T}.$$

Writing the pressures at the transition points D,  $a$ , F, as  $P_{rm}$ ,  $P_{rg}$ ,  $P_{mg}$  respectively, and the temperatures in the same way, we have

$$\log \frac{P_{rg}}{P_{rm}} = \frac{q_r}{2} \left( \frac{1}{T_{rm}} - \frac{1}{T_{rg}} \right), \quad \log \frac{P_{mg}}{P_{rg}} = \frac{q_g}{2} \left( \frac{1}{T_{rg}} - \frac{1}{T_{mg}} \right),$$

$$\log \frac{P_{mr}}{P_{mg}} = \frac{q_m}{2} \left( \frac{1}{T_{mg}} - \frac{1}{T_{mr}} \right);$$

therefore

$$q_r \left( \frac{1}{T_{rm}} - \frac{1}{T_{rg}} \right) + q_g \left( \frac{1}{T_{rg}} - \frac{1}{T_{mg}} \right) + q_m \left( \frac{1}{T_{mg}} - \frac{1}{T_{mr}} \right) = 0,$$

<sup>1</sup> *Proc. Roy. Soc.* 7. 24.

$$\text{or} \quad \frac{q_r - q_m}{T_{rm}} + \frac{q_g - q_r}{T_{gr}} + \frac{q_m - q_g}{T_{mg}} = 0.$$

In this equation  $q_r - q_m$  is the heat evolved when rhombic sulphur is produced from monosymmetric, 2.52;  $q_g - q_r$ , that evolved when rhombic sulphur melts, -11.97;  $q_m - q_g$ , evolved when liquid sulphur crystallizes in the monosymmetric form, 9.45. Finally,  $T_{rm}$  being = 273 + 95.6 and  $T_{mg} = 273 + 120$ ,  $T_{rg}$  is 273 + 114.6, in complete agreement with the observed value.

Now Fig. 9 may be completed, since  $a$  is a point on the line which indicates the equilibrium between rhombic and liquid sulphur, to which line  $\kappa$  also belongs, so that  $\kappa L$  is given as the prolongation of  $a\kappa$ .

*Difference between the phenomena of physical and chemical equilibrium.* Whilst, as we have seen, the phenomena belonging to these two regions may be compared in many respects, the case in which chemical changes take place is distinguished by the indefinite number of changes of state occurring in it, the physical case including three only; ammonium nitrate, e.g., possesses four different crystalline forms below its melting point (168°) bounded by the temperatures 36°, 87°, and 127°<sup>1</sup>. Further, there is the peculiarity mentioned by Neumann<sup>2</sup>, that simple physical change leads in comparatively short time to equilibrium, while in the opposite case that may be arrived at with extreme slowness.

This may be partly due to the time required for orientation, which would explain also, that in the physical case undercooling of the liquid is possible, but not overheating of the solid. In conversions of other kinds both are possible; thus, e.g., rhombic sulphur can retain its form above 95.6° as well as monosymmetric below. This inertia shows itself in fact in the production of states which must be regarded as entirely unstable, since they are converted by contact with the other form, at all temperatures.

<sup>1</sup> Lehmann, *Zeitschr. f. Kryst.* 1. 106.

<sup>2</sup> *Berl. Ber.* 4. 646. 780.

Lehmann therefore distinguishes as enantiotropy the reversible change, as in the case of rhombic and monosymmetric sulphur; and speaks of monotropy in bodies like mercury ditolyl which can assume a second form, e. g. by melting and resolidifying, a form that does not arise directly from the others, but can only suffer the converse change. It must be noted that these two categories may pass into one another by change of pressure, and that, e. g., it appears from Fig. 9 that sulphur is enantiotropic under ordinary circumstances, but above 400 atmospheres the possibility of converting rhombic into monosymmetric sulphur ceases, and the latter form would therefore show the phenomenon of monotropy.

### C. Physical Equilibrium between Two Bodies.

Next may be taken the case in which two substances are brought together, first with the restriction that only physical changes occur, i. e. changes of state of aggregation, and mixture. The complete problem is therefore to know not only what is the result of all possible pressures and temperatures on the system, but also how the ratio of masses affects it. All the possible effects, such as non-miscibility, partial and complete miscibility, apparently pass into one another, for each pair of substances, through change of pressure and temperature, but the cases hitherto investigated have only been studied as representative of the leading types, and these will be brought forward in order of simplicity.

*Without appreciable miscibility.* Let us exclude as far as possible the complicating factor of miscibility and take, e. g., carbon disulphide and water, which, practically, only mix as vapours. The facts are then simple: the liquid and solid bodies behave as if they were present alone, and the mixture of vapour corresponds to both saturation pressures  $P_1$  and  $P_2$ ; the composition, if the molecular weights are  $M_1$  and  $M_2$ , is therefore  $P_1 M_1 : P_2 M_2$ ; the boiling point is the temperature for which  $P_1 + P_2$  is equal to the external

pressure, and so on. Still more simply, the vapour is the sum of the vapours of the two components.

If miscibility is not restricted to the vapours, the case in which only one substance takes up the other may be distinguished from that in which each dissolves the other to a certain extent; the first is familiar, being the case of a solid and a liquid in contact; the second that of a pair of liquids. We will distinguish them as simple and mutual solubility.

### 1. *Simple Solubility.*

In the first place, complete knowledge of the conditions produced by solution involves two problems: knowledge of the solution, and of the vapour rising from it. Attention has usually been devoted to the composition of the solution only. Complete knowledge of the condition produced by bringing the two substances together, however, involves just as much attention to the vapour when it exists, and to its pressure. Two measurements are therefore required, and may be dealt with separately:

#### (a) Measurement of Solubility; (b) Measurement of Vapour Pressure.

(a) *Measurement of solubility.* Starting with the choice of a method, let us adopt the process (one of many) which has of late been used in my laboratory; it was described by Goldschmidt<sup>1</sup>, and is a modification of that of Meyer and Van Deventer<sup>2</sup>, using Witt's stirrer. A Raabe turbine drives the known pattern of stirrer AB, carried by the glass tube c; the rod D along the axis allows the liquid to flow out, when saturation is attained, through a plug of cotton wool F into the weighing tube E. The expression of the results of analysis has often been changed, but it is clearest in terms of the weight. We may choose, then, whether to refer it to 100 parts of solvent (with Gay-Lussac) or to 100 parts of solution (with Etard); the latter has the advantage that the curves representing variability

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 17. 153.

<sup>2</sup> l. c. 5. 559.

with temperature are usually straighter, and also that very great solubilities are more conveniently expressed, since they can obviously not exceed 100, while, according to the first method, they may become infinite.

Let us follow out the results so obtained in certain cases, as far as possible. Silver nitrate is a good example of the effect of temperature, as it was studied by Etard<sup>1</sup> far above

100°, of course in sealed tubes (a weighed amount of water and salt being heated, with shaking, till complete solution). The result was, from 55° on—

$$\gamma = 81 + 0.1328t,$$

from which  $\gamma = 100$  for  $t = 198$ , i.e. at 198° the solubility of silver nitrate is unlimited. This temperature coincides with the melting point of the salt, so that the solubility curve ends in the melting point; the same was found to be the case for some other salts. Note however that this phenomenon is not necessarily general, and a second possibility (of which examples later) exists, the melted salt forming a second layer under the saturated solution. Representing this result graphically with the temperature drawn to the right,  $\gamma$  upwards, and starting from the break that the line ( $\gamma, t$ ) shows at 58° in consequence of a change of crystalline form in the silver nitrate, the question

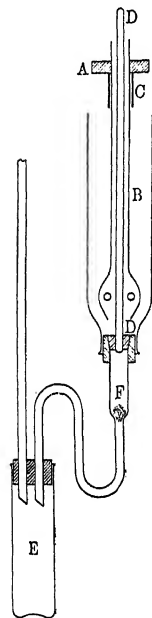


FIG. 10.

arises where the line stops towards the left, i.e. at low temperature. We are concerned here with the behaviour of a saturated solution on cooling: obviously at first salt crystallizes out, but when the temperature sinks to  $-6.5^\circ$ , at which the saturated solution freezes, ice separates, and then the composition does not change any more, as ice and salt separate together and form a solid compound, a so-

<sup>1</sup> *Comptes Rendus*, 108. 176.

called cryohydrate<sup>1</sup> whose composition is that of the saturated solution at the freezing point; the temperature at which constancy occurs is called the cryohydric temperature. The complete line thus runs from the cryohydric point A to the melting point F (Fig. 11). The graphical treatment may be carried further if we remember that it is arbitrary which body is regarded as solvent, and which as dissolved substance; the solution is really a mixture from which one or other component can be separated in the solid form by proper choice of temperature and composition; the mixture is then saturated with regard to that component. AF refers to saturation with respect to

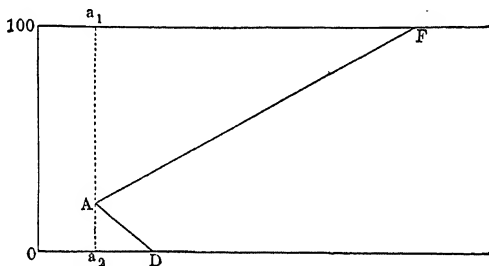


FIG. 11.

silver nitrate. At A another line begins, referring to saturation with the other substance in the solid state, i. e. with ice. This line is to be drawn from A to D ( $0^{\circ}$ , melting point of ice), corresponding to more and more dilute solutions which are saturated with ice at higher and higher temperatures up to  $0^{\circ}$ . But the system of lines FAD now appears in a new light. So far it has been the locus of all possible solutions saturated with salt or ice; it may however be regarded as locus of all the melting points which, starting from ice, lead by addition of silver

<sup>1</sup> Cryohydrates were formerly (as by Guthrie) treated as chemical compounds; that they are mixtures may, however, be seen with the microscope in coloured salts ( $K_2Cr_2O_4$ ); moreover the composition of these so-called hydrates may alter if the freezing occurs under different pressure (Roloﬀ, *Zeitschr. f. Phys. Chem.* 17. 325).

nitrate from D to A and, starting from silver nitrate, lead by addition of water from F to A<sup>1</sup>.

The diagram may now be divided by an appropriately drawn line into areas, each of which has its physical meaning. Working to the right of FAD we have homogeneous mixtures, whatever be the composition, which lead from molten silver nitrate to molten ice, and include all unsaturated solutions; to the left of A, through which the auxiliary line  $a_1 a_2$  is to be drawn, i. e. below the cryohydric temperature, lie the conditions in which the two bodies exist together in solid form. There remain the areas  $a_1 AF$  and  $a_2 AD$ ; they represent conditions unstable, i. e. supersaturated, with silver nitrate ( $a_1 AF$ ) and ice ( $a_2 AD$ ). The latter is usually called undercooled.

Finally, it must be noted that a tacit assumption has been made with regard to the determinations represented in the figure. The solubility and freezing point are dependent on the pressure, although only to a slight extent, as we may see from the previous thermo-dynamical considerations, and from the following examples: ammonium chloride, which dissolves with expansion, loses solubility by 1% for 160 atmospheres; copper sulphate, which contracts on solution, gains solubility by 3.2 % for 60 atmospheres.

The change is so small that it does not come into consideration in ordinary measurements; still even in Etard's measurements, carried out in sealed tubes much over 100°, things are somewhat different, and the above mode of representation can only be regarded as strictly correct if the pressure be taken as the saturation pressure of the solutions considered. With this condition, the lines and points in the diagram are as follows:—

AF, composition of the mixture in presence of silver nitrate and vapour simultaneously.

AD, the same in presence of ice and vapour.

<sup>1</sup> The cryohydric temperature A is obviously the lowest temperature that can be obtained by mixing ice and silver nitrate.

A, the same in presence of silver nitrate, ice, and vapour.

D, temperature at which ice, water, and vapour coexist.

F, temperature at which solid and liquid silver nitrate coexist with their vapours (however highly rarefied).

The special case chosen having been considered in this way, it is hardly necessary to add that any pair of bodies give corresponding results, if only the solution is simple, and the two solid bodies are not miscible (isomorphous) as such. We may take a salt and water, or two salts, or two organic substances, or two metals. The following is an example:—

<i>Naphthalene.</i>	<i>Paratoluidine.</i>	<i>Melting point.</i>
100	0	79.3°
80	20	68.2
50	50	50.3
34	66	38.1
31	69	29.1
29	71	34.6
25	75	35.3
20	80	36.6
0	100	38.9

The freezing points of these mixtures show that up to 69% of paratoluidine, the naphthalene separates out first, at higher concentrations paratoluidine; after this solidification of one of the components, when the temperature 29.1° has been reached, the two separate out together till the mixture solidifies completely.

*Concentration in simple solutions, treated thermo-dynamically.* Bearing in mind the analogy between solutions and gases, the act of solution may be compared with evaporation, and saturation with the occurrence of the maximum pressure. Applying the thermo-dynamic fundamental equation

$$AVdP = q \frac{dT}{T}, \quad (1)$$

let us take as measure of the concentration  $C$  the mass



(kilogram-molecules) in unit volume (cub. metre); mathematically

$$C = \frac{1}{V} \quad \text{and} \quad \frac{AdP}{C} = \frac{qdT}{T}. \quad (2)$$

By applying the laws of Boyle-Gay-Lussac-Avogadro,

$$APV = 2T,$$

we get

$$AP = 2CT \quad \text{and} \quad AdP = 2CdT + 2TdC.$$

Introducing these in (2) we have

$$\frac{d \log C}{dT} = \frac{q - 2T}{2T^2},$$

in which  $q - 2T$  has a simple physical meaning, since  $q$  is the heat of evaporation (of a kilogram-molecule) including the external work done in the process. Since that work  $APV$  is by the above equation  $= 2T$ , it follows that  $q - 2T$  is precisely the heat required to effect the change of state only; it may be described as the internal latent heat, and written  $Q$ , thus:

$$\frac{d \log C}{dT} = \frac{Q}{2T^2}.$$

In applying this to dilute solutions everything remains the same, except that  $Q$  is here the heat directly measured in the calorimeter during simple solution, since no external work is done. The following examples<sup>1</sup> may serve as test, only non-electrolytes being taken, since Avogadro's law only applies to them. The equation is used in the integral form,  $Q$  being assumed constant, which is approximately the case:

$$\log \frac{C_1}{C_2} = \frac{Q}{2} \left( \frac{1}{T_2} - \frac{1}{T_1} \right).$$

Since only the quotient of the concentrations comes in, the unit in which that quantity is expressed may be chosen arbitrarily.

<sup>1</sup> Van 't Hoff, *Kongl. Svenska. Akad. Handl.*, 1886, p. 38.

<i>Substance.</i>	<i>Concentration.</i>	<i>Temperature.</i>	$\frac{Q}{1000}$ <i>calculated.</i>	$\frac{Q}{1000}$ <i>observed.</i>
Succinic acid	2.88	0		
"	4.22	8.5	6.9	6.7
Benzoic acid	0.1823	4.5		
"	2.1931	75	6.7	6.5
Salicylic acid	0.16	12.5		
"	2.44	81	9	8.5
Boric acid	1.947	0		
"	2.92	12	5.2	5.6
Phenol	7.12	1		
"	10.2	45	1.2	2.1
Mercuric chloride	6.57	10		
"	11.84	50	2.7	3

In order to make the fundamental equation (1) generally applicable, it would be necessary to find the relation between concentration and osmotic pressure for solutions that are not dilute. That is at present unknown. But if it be introduced in the general form  $(\frac{\partial P}{\partial C})_T$  a result is arrived at that is worthy of attention. We can then divide into two parts the increase in osmotic pressure with temperature  $\frac{dP}{dT}$  as it occurs in equation (1), one due to change of temperature alone  $(\frac{\partial P}{\partial T})_C$ , and one due to the accompanying change of concentration. Thus

$$\frac{dP}{dT} = \left(\frac{\partial P}{\partial T}\right)_C + \left(\frac{\partial P}{\partial C}\right)_T \frac{dC}{dT}.$$

The relation between concentration and temperature then appears in the form

$$\frac{dC}{dT} = \frac{\frac{dP}{dT} - \left(\frac{\partial P}{\partial T}\right)_C}{\left(\frac{\partial P}{\partial C}\right)_T},$$

and by applying equation (2)

$$\frac{d \log C}{dT} = \frac{q - q_c}{AT \left(\frac{\partial P}{\partial C}\right)_T} = - \frac{Q}{AT \left(\frac{\partial C}{\partial T}\right)_T},$$

in which  $q$  is the heat absorbed when a kilogram-molecule dissolves to saturation in the pure solvent,  $q_c$  that absorbed when the pure solvent is transformed into saturated solution (by mixture with an infinite quantity of it).  $q - q_c$  or  $Q$  is therefore the heat which would be absorbed, theoretically, if the substance were dissolved in its saturated solution, a quantity which may be arrived at as a limiting value, and so may be called the 'ideal heat of solution.' It is important, and indeed so far the leading result of the above equations, that the increase of solubility with the temperature,  $\frac{d \log C}{dT}$  or  $\frac{dC}{dT}$ , is determined as

to sign by  $Q$ ; since  $\frac{\partial P}{\partial C}$ : the increase of osmotic pressure with the concentration, is positive. As example, it may be mentioned that, as the great majority of solids dissolve with absorption of heat, their solubility increases with the temperature, and in the opposite case decreases. The less common cases where the converse is true are for that reason noteworthy, and one or two may be remarked on here<sup>1</sup>.

1. Lime decreases in solubility with rise of temperature; the same is true of calcium propionate, butyrate, valerate; further of barium valerate and capronate, and of zinc butyrate. In all these cases the heat of precipitation is negative, i. e. heat is evolved on solution.

2. Some substances, such as gypsum and some of the above-named organic salts, show a maximum of solubility, so that at that temperature a reversal of sign occurs in the change of solubility. That goes hand in hand with a reversal of sign in the heat of precipitation; if the latter is  $Q_T$  at one temperature and  $Q_{T+t}$  at another, a cyclic process without performance of work may be imagined in which salt is precipitated at  $T$ : heat  $Q_T$ ; salt and solution are heated by  $t^\circ$ : heat  $-C't$ ; the precipitated salt dissolved at  $T+t$ : heat  $-Q_{T+t}$ ; and the solution cooled to  $T$ : heat  $C''t$ , in which  $C'$  and  $C''$  are the specific heats of salt

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 4. 63-65.

+ solution separately and of salt + solution dissolved. Consequently

$$Q_T + t(C'' - C') = Q_{T+t}.$$

Although  $C'' - C'$  is in general small, yet if  $Q$  is not large, it may cause  $Q$  to become zero at some temperature, and afterwards to change its sign. For gypsum, according to Berthelot, that is the case at about  $35^\circ$ , where  $Q$  changes from positive to negative: in agreement with the observed maximum of solubility at that temperature.

The reverse—a minimum of solubility—occurs now and then, e.g. in zinc butyrate, and is accompanied by the corresponding thermal singularity<sup>1</sup>.

3. Sudden changes of solubility also occur, which depend on a modification of the dissolved substance at a definite temperature; the substance may change its crystalline form, it may melt, or it may lose water of crystallization. Since these changes are all accompanied by absorption of heat, they all affect the heat of precipitation in the same sense, making it smaller, and do the same with the value of  $\frac{dC}{dT}$ , which at such a point shows a bend downwards. If this goes so far as to change a positive into a negative heat of precipitation, the increase of solubility changes into a decrease, as has long been known to be true of sodium sulphate at  $32.6^\circ$ . More recently Etard's researches, carried to high temperatures, have shown that almost all sulphates (e.g. copper sulphate), after increasing in solubility to a certain temperature, lose water of crystallization, and begin then to diminish in solubility, till finally they become almost insoluble. Just the opposite case to that of silver nitrate, of which the solubility finally becomes infinite.

#### (b) Vapour Pressure of Simple Solutions.

(a) *Maximum pressure: application of thermo-dynamics.*  
The consideration of the vapour present at equilibrium,

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 4. 63.

consequently also during the act of solution, obviously necessary as it is to a complete insight into the phenomena of equilibrium, becomes all the more prominent for being amenable to thermo-dynamics. Whilst the equations referring to solution and to evaporation take the same form, if only the osmotic pressure be introduced into the one, the gas pressure into the other, the latter have an advantage, since the gas pressure can be easily dealt with by experiment, and the equations below may thus be verified.

For the maximum pressure of the saturated solution the equation

$$\frac{d \log p}{dT} = \frac{q}{2T^2}$$

may be applied, since for all aqueous solutions yet investigated the vapour is sufficiently rare to follow the usual laws of gases. The meaning of  $q$  requires careful definition, being the heat of condensation of a kilogram-molecule, i.e. 18 kilograms of water, but with the condition that it condenses to form saturated solution. This quantity of heat may be divided into two parts: first  $q_1$ , which is absorbed when the required quantity of saturated solution is separated into salt and 18 kilograms of water; second, the latent heat of evaporation  $L$  of the water. The former quantity is the heat given out on saturation, which is usually negative: so for clearness the sum may be written  $L - q_1$ . The value of  $L$ , in general large compared with  $q_1$ , makes the sum constantly positive, so that, as might be expected, the maximum pressure of the solution increases with temperature. There is, however, a possible singularity. If the solubility is very great,  $q_1$  might accordingly increase till it equalled and exceeded  $L$ , i.e. the pressure curve would at first rise with the temperature, rapidly to begin with, then more slowly, till at last it sank. This is the case with silver nitrate, for the composition of the solution eventually at  $198^\circ$  becomes that of the salt alone, so that the pressure, which rises rapidly to well over  $100^\circ$ , sinks again at  $198^\circ$  to almost zero.

The fact has been directly observed for hydrated calcium chloride ( $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ), for which the following pressure measurements are recorded<sup>1</sup>:—

20°	25°	28.5°	29.5°	30.2°
5.62	6.7	7.02	6.91	6.7

with a maximum at 28.5°. The experiment shows that the total latent heat is 0, suffering a reversal of sign at that temperature; moreover the calculated and observed values of  $\frac{d \log p}{dT}$  agree:

<i>t</i>	<i>p</i> (mm. of bromo- naphthalene)	<i>q</i>	$\frac{d \log p}{dT}$ (calculated).	$\frac{d \log p}{dT}$ (observed).
0°	18	40807	0.0626	0.105
10	32	30490	0.0545	0.047
20	52	17145	0.0438	0.043
25	62	8220	0.0305	0.026
27	64	2480	0.0122	0.012
28	64.5	1575	0.0094	+
28.5	65	210	0.0014	0
29	64.5	— 1400	— 0.012	—
29.5	64	— 3700	— 0.045	—
30	61	— 8900	∞	∞

As pointed out for silver nitrate, the maximum pressure, which first rose gradually, sinks at last to zero (or more strictly, to the pressure of the salt at its melting point). The pressure curve must therefore, after rising like AM (Fig. 12), pass through a maximum M, and descend to OT in F. For greater clearness let us consider the question as to the value of  $\frac{dP}{dT}$  at the end point F. Then the value of *q*, which has become negative on account of the heat of solution, eventually, since the solubility becomes infinite at the melting point, becomes infinitely great in the negative sense, which therefore makes

$$\frac{d \log p}{dT} \text{ and } \frac{dP}{dT} = -\infty,$$

<sup>1</sup> Bakhuis Roozeboom, *Rec. des trav. Chim.* 8. 78.

i. e. the pressure curve becomes vertical on reaching F, as shown in Fig. 12.

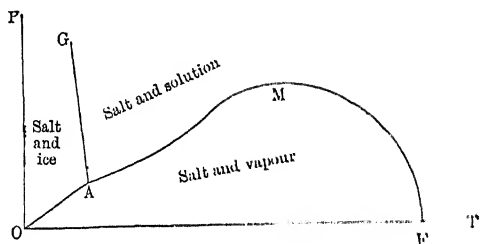


FIG. 12.

Let us complete this graphical representation, going back to the cryohydric point A, and showing the alteration of that point with increase of pressure by AG; then the plane of the figure is divided into areas, of which, again, each has its meaning.

OAMF shows the conditions for the simultaneous existence of salt and vapour, OAG for salt and ice, OAM for salt and solution.

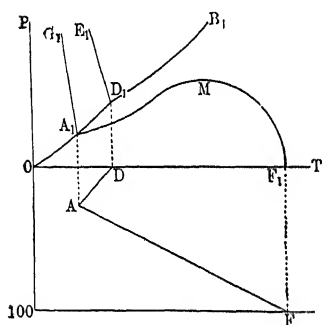


FIG. 13.

The lines correspond to the following states: AMF, salt, vapour, and solution; AG, salt, ice, and solution; OA, salt, ice, and vapour. At A, salt, ice, solution, and vapour are possible together, and that point is therefore a quadruple point; it is practically the same as

the cryohydric point, only with the reservation that it is the cryohydric point, not for atmospheric pressure, but for the maximum pressure of the saturated solution.

The above diagram is so far incomplete that it shows only saturated solutions; in order to introduce the unsaturated, and that up to their extreme limit—water, a combination of Fig. 12 with Figs. 11 and 4 is necessary, in the

form of a projection (Fig. 13). Take DAF, Fig. 11, showing the composition for horizontal plane; then  $E_1D_1B_1$ , the pressure diagram, Fig. 4, may be reproduced on the vertical plane. D then lies on the axis OT; A is given by the projections  $A_1$  and A. The pressure diagram  $E_1D_1B_1$  refers, as Fig. 4 did, on the left of  $E_1D_1$  to ice, right of that to water.  $D_1$  corresponds to the pressure of pure water at the freezing point, and consequently lies above  $A_1M$ , which refers to the saturated solution;  $D_1$  also lies in the continuation of the curve  $OA_1$ , since that, like  $A_1D_1$ , gives the pressure of ice; from  $D_1$  to the right lies the vapour pressure curve for water. Further, the boundary between water and ice,  $D_1E_1$ , may be drawn from  $D_1$  upwards, and from  $A_1$  the line  $A_1G_1$  of cryohydric pressure, which is given on the horizontal plane by a line corresponding to the composition of the cryohydric solutions for different pressures. The new areas, given only by the projection, relate to conditions not previously taken into account:

FMADB<sub>1</sub>, unsaturated solution and vapour, bounded by AMF for the saturated solution, DB<sub>1</sub> for water, and AD for the freezing point.

G<sub>1</sub>ADE<sub>1</sub>, unsaturated solution and ice, bounded by G<sub>1</sub>A for the cryohydric state, E<sub>1</sub>D for water, and AD for the melting point.

(β) *Pressure of the unsaturated solution.* The theorems and results developed so far refer to the state of so-called saturation, at least so far as they have been followed out thermo-dynamically; only in the graphical representation finally adopted was a place found for the unsaturated condition. This place may be exactly defined by a series of measurements with successively greater concentrations. Each pressure curve so found must correspond with an equation

$$\frac{d \log p_1}{dT} = \frac{q}{2T^2},$$

in which the value of  $q$  must be considered separately in each case, and stands for the heat developed when 18 kilograms of vapour, after condensation—with evolution of



heat  $L$ —is converted into the solution in question (by mixture with an infinite quantity of it) with evolution of heat  $l$ ; thus

$$\frac{d \log p_1}{dT} = \frac{L + l}{2T^2}.$$

If the heat of dilution  $l$  be neglected, as may be done in the case of very dilute solutions, then by the aid of the equation for the solvent,

$$\frac{d \log p}{dT} = \frac{L}{2T^2},$$

we get  $\frac{d(\log p - \log p_1)}{dT} = \frac{d(\log \frac{p}{p_1})}{dT} = 0$  or  $\frac{p}{p_1} = \text{constant}$ .

This is Babo's law, that the ratio of the vapour pressures of solvent and solution does not change with the temperature, true only as a limit for increasing dilution.

The value of this ratio may be found by means of a simple cyclic process. From a solution containing 1 kilogram-molecule of dissolved substance to  $a$  kilogram-molecules of solvent,  $a$  kilogram-molecules of solvent are withdrawn osmotically by expenditure of work  $2T$ . By evaporation at  $p$ , expansion till the pressure falls to  $p_1$ , and condensation at  $p_1$  in contact with the solution, the cycle is completed, and the work in evaporation and condensation cancelling, we have left the work of expansion

$$2aT \log \left( \frac{p}{p_1} \right).$$

As the cycle is at constant temperature, the net work accomplished must be zero, and we have the equation

$$2T = 2aT \log \left( \frac{p}{p_1} \right), \quad \text{or} \quad a \log \left( \frac{p}{p_1} \right) = 1.$$

In the limiting case

$$\log \left( \frac{p}{p_1} \right) \text{ becomes } \frac{(p - p_1)}{p}, \quad \text{and} \quad \frac{p - p_1}{p} = \frac{1}{a},$$

corresponding to Raoult's well-known law, that the relative lowering of vapour pressure is equal to the ratio between the number of molecules of dissolved substance and solvent.

## 2. *Mutual Solubility.*

In accordance with the order chosen, in which first a pair of substances which practically do not mix was briefly dealt with, then the case of simple solubility, in which only one of the two bodies (the liquid, the solvent) takes up the other (the soluble solid), we come now to the third case, in which each substance takes up the other. This third case is known to be that of many pairs of liquids, e.g. ether and water, so that the consideration of it follows naturally on such observed instances. The composition of the two liquid layers will be taken first, then that of the vapour.

(a) *Composition of the two liquid layers.* The fundamental rule here is that the composition of the two layers is independent of the mass of the components, provided only that neither of the layers is reduced to the point of vanishing, and that there is opportunity for the formation of vapour. Let us consider, e.g., what happens when ether and water are mixed in any proportions. Starting from water alone, addition of ether forms a solution of ether in water, more and more concentrated. Finally saturation occurs, and a second layer is formed of ether, in which the maximum of water is dissolved. On further addition of ether, the amount of the aqueous layer gradually diminishes, while that of the other increases; but—and this is the chief point to note—the composition of each layer remains that corresponding to saturation, until so much ether is added that the aqueous layer disappears; then we get a more and more dilute solution of water in ether.

This may be expressed graphically by the annexed Fig. 14. All possible states, from 100% water to 100% ether, are shown along AD and AE: on AD the proportions taken, on AE the mixtures produced; AB then stands for the unsaturated solutions of ether in water, and bisects

the angle  $EAD$ , since  $AD=AE$ . At  $B$  the second layer appears, of composition expressed by  $B_1$ ; that composition

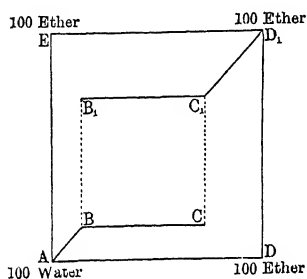


FIG. 14.

remains unchanged, corresponding to the horizontal course of  $BC$  and  $B_1C_1$ , till finally the solutions  $C_1D_1$  of water in ether pass into pure ether. An easily overlooked point is tacitly assumed in this, viz. the opportunity for evaporation. If vapour is not present, the composition of the layers changes according

to the pressure exerted on the liquid; if vapour can be formed, and only water and ether, not air be present, the pressure is constant, viz. that of a saturated solution of ether in water, or water in ether.

The study of the behaviour of a pair of liquids thus comes essentially to be the determination at different temperatures of the ratios expressed by  $BC$  and  $B_1C_1$ .

Take, e.g., a series of Alexejeff's<sup>1</sup> measurements. The researches were carried out by heating a weighed mixture of, say, water and aniline, in a sealed tube, till complete mixture took place, i.e. till the point  $B$  was reached. The following results were obtained:—

Temperature	16°	55°	77°	142°	156°	164°	157°	68°	39°	25°	8°
% aniline	3.1	3.6	5.3	14	21	37	74	94	94.6	95	95.4

The results are expressed by Fig. 15; the composition of the two layers is shown by  $ABC$ , the temperature along  $OT$ ; the point  $B$ , reached at  $165^\circ$ , corresponds to complete miscibility. This completes the list of possibilities so far considered thus:

- Non-miscibility (more or less general for solids).
- Simple solubility: one body only takes up the other (more or less general for presence of a solid and a liquid together).

<sup>1</sup> *Ann. de Chim. et de Phys.* 1886, 28. 305.

- (c) Mutual solubility (two liquids).  
 (d) Complete miscibility (general for gases).

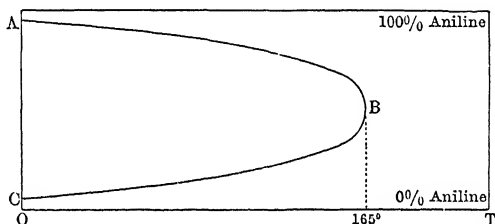


FIG. 15.

It may be added that the temperature of complete miscibility for liquid mixtures is comparable to the critical temperature for single liquids<sup>1</sup>. Probably it and the accompanying relations of pressure and composition will play as important a part in considering the properties of mixtures, in connexion with temperature, as the critical temperature does in the case of liquids and gases.

The above case is that of most liquid mixtures, such as have a temperature of mixing upwards, but the opposite case possesses a peculiar interest also.

Dimethylamine and water separate on rise of temperature, reaching complete miscibility on sufficient fall of temperature. The thermo-dynamic considerations explained in connexion with simple solubility at once show that the act of mixing must in this case be accompanied by evolution of heat, so it may be thought that chemical action, such as the formation of a hydrate, takes place, although no proof of that exists; but the existence of a dimethylamine hydrate is not improbable. If that is the reason, it might be expected that rise of temperature, which opposes the formation of this exothermic hydrate, would again bring about an increase of solubility and lead to another limit of miscibility B. The complete phenomenon would then be such as shown in Fig. 16.

<sup>1</sup> Orme Masson, *Zeitschr. f. Phys. Chem.* 7. 500; Natanson, l. c. 9. 27.

The minimum of solubility ( $\alpha$ ) to be expected has been observed in certain mixtures, such as water and butyl alcohol.

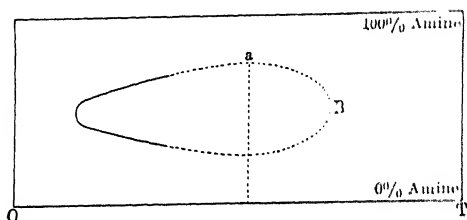


FIG. 16.

(b) *Composition of vapour and its pressure.* In the case of two liquid vapours and the vapour over them, a point is to be noted that is apparent *a priori*, and has been partly verified by experience. The vapour is in equilibrium with both liquid layers; in other words, a saturated solution of ether in water, and a saturated solution of water in ether, will send out identical vapour, care only being taken that the evaporation does not cause any change in the composition of the liquids. The identity of course extends not only to the total pressure, but to the partial pressure of each component. Only the first has been verified. In the case of ether and water, Konowalow<sup>1</sup> found at 19.8

Ethereal layer . . .	Saturated pressure, 432.2 mm.
Aqueous layer . . .	„ „ 430.1 „

### 3. Complete Miscibility.

Complete miscibility, the last stage in the phenomena of mixture, requires a somewhat more thorough treatment, especially with reference to fractional distillation, which is conditioned by the rules here obtaining. Three essential points are to be attended to:—

1. The composition of the vapour which rises from the liquid mixture on boiling.

<sup>1</sup> *Wied. Ann.* 14. 34, 219.

2. The composition of the vapour which is in equilibrium with the mixture at the boiling point.

3. The composition of the vapour which corresponds to the mixture of lowest boiling point.

On the composition of the vapour which is given off on boiling only this can be said, that it is not necessarily the same as that which is in equilibrium with the liquid mixture. The latter will clearly be formed only when the distillation is slow enough, and will be of the composition  $P_1M_1 : P_2M_2$ , where  $P_1$  and  $P_2$  are the partial pressures of the components,  $M_1$  and  $M_2$  their molecular weights; finally  $P_1 + P_2 = D$ , where  $D$  is the external pressure under which the boiling takes place.

The composition of the vapour corresponding to the mixture of lowest boiling point is of essential importance for fractional distillation, since, whatever the construction of the apparatus used may be, it is always arranged to collect the liquid or mixture of lowest boiling point.

With the aid of Konowalow's measurements we are able to particularize this further. Systematic determination of the pressures of different mixtures leads to the demarcation of three types, which also constitute the leading cases in distillation.

1. The first case, of which propyl alcohol (P) and water (w) may be taken as an example, shows a maximum of vapour pressure at a certain composition—*a* at 88° in Fig. 17.

2. The second case, e.g. methyl alcohol (M) and water (w), shown in Fig. 18, does not possess the maximum.

3. The third case, of which formic acid (A) and water (w) may be chosen as an example, has a minimum of vapour pressure—*a*, Fig. 19.

The question may now be readily answered: When does a given mixture of the liquids considered boil? It is at the temperature for which the pressure appearing in the diagram becomes equal to the external pressure; thus, for the external pressure  $p$  (Fig. 17) the mixture of composition

(b) would boil at  $35^\circ$ . The composition of the vapour produced, and consequently of the distillate, cannot be found from Konowalow's results.

By fractional distillation, as we have seen, the liquid, or mixture of lowest boiling point, i.e. of highest vapour pres-

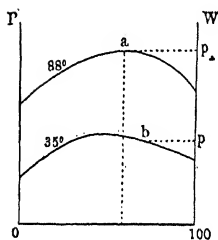


Fig. 17.

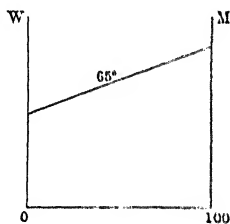


Fig. 18.

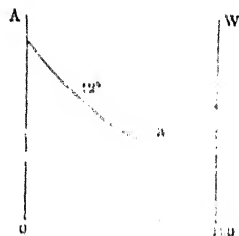


Fig. 19.

sure, is obtained; at a pressure  $p_a$  (Fig. 17) perfectly conducted fractionation of a mixture of propyl alcohol and water would give a distillate of the composition  $a$ ; the result would be decomposition of the liquid to be fractionated, into a part of composition  $a$  and a residuum of higher boiling point, consisting either of water or of propyl alcohol, according as the original liquid contained more of the one or the other liquid than corresponds to  $a$ . Complete separation is therefore not possible.

How far reduction of pressure may cause a favourable change in this respect depends on whether at lower temperatures the maximum of vapour pressure answers to a composition further removed from that of the mixture to be fractionated. Something may be predicted on that point from a knowledge of the vapour pressure curves and of their latent heat of evaporation. It may be added that the method of fractional distillation with steam<sup>1</sup> lately proposed is equivalent to working at low pressure.

The second case—that of methyl alcohol and water—is the simplest, with regard to the possibilities of fractional

<sup>1</sup> *Journ. f. Prakt. Chem.* 39. 39.

distillation. One of the two liquids—in this case methyl alcohol—goes over first; the other remains behind, or distils last.

In the third case it is necessary to distinguish whether the liquid has a composition that lies to the left or the right of the pressure minimum; in the one case the liquid on the left—here formic acid—distils, in the other water; in both a mixture corresponding to the minimum vapour pressure remains behind. This agrees, therefore, with the first case, in the impossibility of complete separation; but here the unfractionated mixture has the highest boiling point, in the other case the lowest.

Apart from fractional distillation, the comparison of the three types may be looked at in another way, if the partially miscible and immiscible cases be considered too. All five cases form a series. In the case of immiscible liquids the pressure diagram may be drawn *a priori*, if at *a* (Fig. 20) we draw *ab* for the pressure of one component, and at *c* draw *cd* for the pressure of the other component; all the mixtures will then have the pressure  $ae = ab + cd$ . If partial mixture occurs the line *beed* is altered: the verticals *be* and *ed* change to the gradual increase shown by *be<sub>1</sub>* and *e<sub>1</sub>d*, and these are joined by horizontal *e<sub>1</sub>e<sub>1</sub>* referring to the two layers of liquid. Since the pressure of each component in the partial mixture must be less than that of the same substance by itself, the line *e<sub>1</sub>e<sub>1</sub>* must lie below *ee*.

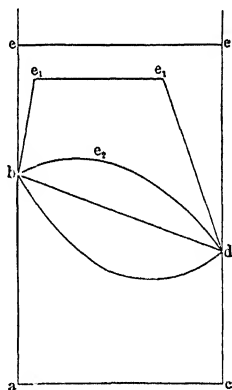


FIG. 20.

The case in which two layers are formed, with its accompanying maximum of pressure, leads to the third, in which completely miscible liquids, such as propyl alcohol and water, give a maximum of pressure for a definite composition as shown by *be<sub>2</sub>d*. From this consideration it is



obvious how such pairs of liquids occur as give constant boiling mixtures of the lowest boiling point: taking, for instance, water with the members of a homologous organic series of alcohols, acids, &c. (since the higher members do not mix with water, but the lowest often do), then the pairs with low boiling fractions are composed of water and the limiting member which is miscible with it—allyl alcohol, propyl alcohol, &c. The phenomenon is most striking when the two liquids have boiling points near together, i.e. the lowering of the boiling point for the constant boiling mixture is greatest. It is clear from the above that we are not here concerned with a hydrate.

The case of formic acid and water, in which the constant boiling mixture has the highest boiling point, suggests chemical action—formation of a hydrate more. The expulsion of one of the two bodies till a constant composition is reached, is in itself suggestive of combination in definite proportions, especially as a marked rise of boiling point often does result from undoubted chemical action, as in the case of  $\text{H}_2\text{O}$ ,  $\text{SO}_3$ , and  $\text{H}_2\text{SO}_4$ . Still it was shown, by Roscoe, that even such constant boiling mixtures are not real hydrates, since the mixture of, say,  $\text{HNO}_3$  and  $\text{H}_2\text{O}$ , with highest boiling point, alters its composition with change of pressure. But equilibria in which hydrates do take part may occur.

Since complete data on the pressures of the mixtures in such cases of fractional distillation are wanting, a rough insight into the phenomenon may be obtained by regarding immiscibility as the limiting case. In that limiting case, the mixture passes over in the ratio  $P_1M_1 : P_2M_2$  ( $P_1$  and  $P_2$  the vapour pressures,  $M_1$  and  $M_2$  the molecular weights), and one of the two liquids remains behind. The further  $P_1M_1 : P_2M_2$  is removed from unity the more favourable are the conditions. It follows that if  $P_1$  and  $P_2$  are known for different temperatures, an indication is obtained on the effects of distillation under changed pressure. Further, some information is obtained as to which are favourable

and which unfavourable cases for the fractionation of homologues. There  $P_1$  is always  $> P_2$  and  $M_1 < M_2$ ; the two latter quantities will, however, bear a ratio nearer to unity as the molecular weight becomes greater, so that for such cases  $\frac{P_1 M_1}{P_2 M_2}$  will differ the most from unity. Thus the prospect is comparatively favourable in the case of homologous iodides, unfavourable for hydrides.

#### 4. *Interesting Special Cases. Benzoic (and Salicylic) Acid and Water.*

Whilst the various types of physical mixture have been dealt with above, from complete immiscibility to complete miscibility, two special cases may now be taken, the first of which is that of benzoic acid and water. Here we are essentially concerned with the fact that in the same pair of bodies, immiscibility may be gradually transformed into simple, then mutual solubility, and finally into complete miscibility. In the previous cases the transformation is effected by rise of temperature: below the cryohydric temperature ice and benzoic acid are practically without action on one another; on fusion of the ice, one-sided solution of the benzoic acid begins; later, on fusion of the acid, mutual solubility occurs, changing eventually to complete miscibility. Alexejeff's<sup>1</sup> investigations on this point have settled that benzoic acid, after an increase of solubility with rise of temperature has shown itself, melts at  $90^\circ$ , i.e.  $31.4^\circ$  under the usual melting point  $121.4^\circ$ . This is, therefore, not simple fusion, but the formation of a layer rich in benzoic acid (95.88% acid to 4.12% water). The lowering of the melting point in question might be calculated from the formula  $\frac{0.02T^2}{W}$ , if only  $W$ , the melting point of benzoic acid, were known. The upper aqueous layer contains 78.8% water and 21.2% acid. The two layers approach one

<sup>1</sup> *Ann. d. Phys. u. Chem.* 1886, 28. 308.

another in composition till at  $116^\circ$  they become identical: that is, complete mixture occurs.

Graphically, the representation (Fig. 21) is made up essentially of a combination of the earlier Fig. 11 and Fig. 15.

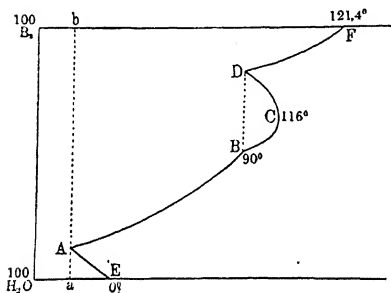


FIG. 21.

The solubility curve AB, beginning at the cryohydric point A, stops at B with the formation of layers. The expression of the layer forming is, as in Fig. 15, the line BCD, in which D is the layer richer in acid formed at  $90^\circ$ , C is total miscibility. The curve may

be completed by EA, which shows the freezing, or melting, point of ice containing more and more benzoic acid, and on the other side by FD, showing the melting point of benzoic acid containing more and more water.

Finally it may be remarked that, again, the diagram may be divided into several areas of which each has a definite meaning:

To the right of EABCDF, homogeneous liquid mixture of benzoic acid and water.

Left of  $aab$ , ice and benzoic acid unmixed.

AEA, undercooled solutions which freeze with formation of the solutions corresponding to AE.

ABDFb, solutions supersaturated with benzoic acid which form, with separation of acid, the saturated solutions corresponding to AB and DF.

DCB, unstable mixtures that separate into two liquid layers represented by BC and DC.

One other remark may be made in comparison of this diagram with that of  $\text{AgNO}_3$  and water (Fig. 11): BCD is there either absent, or so small that it has escaped observation.

5. *Interesting Special Cases. Solid Solutions or Isomorphous Mixtures.*

Although in solids miscibility is reduced to a minimum, yet it so often occurs that one solid takes up another that the name solid solution seems appropriate, in order to bring the phenomena to be expected in such cases into line with others more completely studied. Complete miscibility then answers in many respects to the case of solids which are so far isomorphic that mixed crystals of all compositions are possible, as with the alums. It is interesting to note that partial miscibility also has its analogy amongst pairs of solids, i. e. isomorphism may occur, but not so far as to render all compositions of crystal possible, and in that case we may have so-called isodimorphism, in which a certain intermediate region is missing in the series of possible mixtures: tetragonal  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ , for instance, can take up rhombic  $\text{BeSeO}_4 \cdot 4\text{H}_2\text{O}$  to the composition 7.33  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O} : \text{BeSeO}_4 \cdot 4\text{H}_2\text{O}$ ; more selenate cannot be taken up, or rather miscibility ceases, until the ratio 4  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O} : \text{BeSeO}_4 \cdot 4\text{H}_2\text{O}$  is reached, when the form is rhombic like the pure selenate. This is exactly represented by the diagram Fig. 14. AB represents the series of mixed crystals which starting from pure beryllium sulphate  $\infty : 1$  passes through all ratios to 7.33 : 1; if the solution contains the salts in a ratio intermediate between B and C, i. e. between 7.33 : 1 and 4 : 1, crystals are deposited of the two forms corresponding to those compositions; when more selenate is present the mixed crystals represented by  $c_1D_1$  are produced, ending with the pure selenate 0 : 1. Retgers<sup>1</sup>, who studied this phenomenon—discovered by Topsoë—thoroughly in several cases, represents the results by a formula of the following kind:

(reg.) 18.2%  $\text{AgClO}_3 - \text{NaClO}_3$  28.5% (quadr.),

which expresses that sodium chlorate mixes with silver

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 4. 593.

chlorate to form regular crystals as far as the composition  $18.2\%$   $\text{AgClO}_3$ ,  $81.8\%$   $\text{NaClO}_3$ ; then a stage is wanting, in which more  $\text{AgClO}_3$  would be present, till  $28.5\%$   $\text{NaClO}_3$  and  $71.5\%$   $\text{AgClO}_3$ , which crystallize together, but in the quadratic system, the same being true with increased content of  $\text{AgClO}_3$  up to the pure salt. It may be added that, as with the mutual solubility of liquids, the result just mentioned in general varies with the temperature; when the two mixtures are in the same crystalline form the partial miscibility probably changes into complete isomorphism at some definite temperature; otherwise dimorphism occurs for a certain composition of the mixture, and afterwards spreads till it reaches the end members of the series at a temperature which is to be regarded as the transition point.

Finally the important result must be mentioned, which Küster<sup>1</sup> arrived at in his researches on isomorphous mixtures, with regard to their melting point. Whilst in Fig. 11 the melting points of the bodies D and F are lowered by mutual mixture, falling eventually to the minimum A, in the isomorphic series melting points of mixtures are found corresponding to a straight line between D and F.

#### D. Chemical Equilibrium between Two Substances.

##### 1. *Maximum Vapour Pressure of Hydrates.*

To state the principal phenomena in this branch of the subject in gradual development, let us choose the simplest cases, so as to gain a comprehensive view of the somewhat complicated facts involved.

We may take as a simple and well-investigated case, typical of others, the behaviour of salt-hydrates; i.e. the behaviour of salt and water, in cases in which a combination of the latter as water of crystallization is possible.

Such hydrated salts are known to give off water as vapour, in vacuo. The rule is that loss of water occurs till,

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 5. 601, 8. 577, 12. 508, 15. 86.

for a given salt and given temperature, a certain vapour pressure is reached, independent of the amount of water previously given off as vapour. This law has been most sharply tested by Andrae<sup>1</sup>, who with an apparatus of the annexed

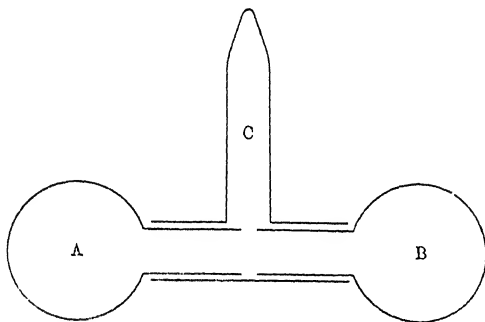


FIG. 22.

form (Fig. 22) compared the vapour pressures of two specimens of strontium chloride,  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ , of which the one in A had been dehydrated slightly, that in B largely, corresponding to the composition  $\text{SrCl}_2 \cdot 4.69\text{H}_2\text{O}$  and  $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ . No transfer of vapour was detected by weighing, after the apparatus had been left in a drawer for months, which would have been the case if the pressures had been different on the two sides, the more so as the apparatus was evacuated by means of the T-piece at the side.

The vapour pressure of water of crystallization has been measured, and most accurately, by Frowein<sup>2</sup>, with a gauge represented in Fig. 23. The one reservoir, *e*, contains sulphuric acid, the other, *d*, is filled with the fully dried salt (best deprived of half a molecule of water) in fine powder; the U tube, bent as close together as possible, contains olive oil, and the whole

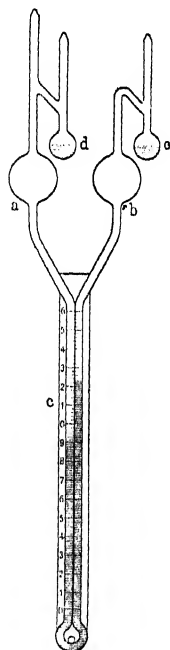


FIG. 23.

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 7. 241.

<sup>2</sup> *I. c. I. 1*, 362, 7. 260, 17. 52.

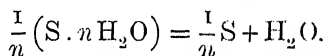
apparatus is evacuated with a mercury pump and sealed off. The difference of level of the oil shows the vapour pressure to be measured, and can be estimated to a tenth of a millimetre by the milk-glass scale attached. The whole is kept in a Herwig water-bath at a constant temperature, till the constancy of the level of oil shows that the equilibrium pressure is reached. The following tabular summary of results may be given, the pressures being reduced to millimetres of mercury:—

$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$					
17.28°	10.531	18°	8.406	19.7°	5.61	13.95"	2.993	18.25"	2.97
27°	21.575	29.95°	22.389	37.55°	19.86	39.7"	21.701	43.45"	21.117

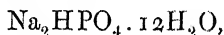
It follows at once from these data that the maximum pressure rises with the temperature. The law of variation may be arrived at thermo-dynamically in the same way as for the maximum pressure of a liquid such as water (cf. p. 21), and is given by the equation

$$\frac{d \log p}{dT} = \frac{q}{2T^2},$$

in which  $q$  is the latent heat of evaporation per kilogram-molecule (i.e. 18 kilograms of water) when the vapour is produced from the hydrate according to the equation



Applying the equation to the observations on



and assuming  $q$  to be constant,

$$\log_e p = -\frac{q}{2T} + \text{const.};$$

or, in common logarithms,

$$\log_{10} p = \frac{q}{4.6T} + \text{const.} = B - \frac{A}{T}.$$

From the values for 6.8° and 27° it follows that

$$\log_{10} p = 10.6213 - \frac{2786.23}{T},$$

whence we get the table:

Temp.	<i>p</i> obs.	<i>p</i> calc.
6.8°	4.606	(4.606)
10.82	6.383	6.386
15	8.837	8.85
17.28	10.531	10.55
20.15	13.087	13.093
23.02	16.191	16.184
27	21.575	(21.575)

The agreement is very good, and a further control may be obtained from the fact that

$$A = \frac{q}{4.6}, \text{ whence } q = 12817.$$

This is the amount of heat absorbed when acid sodium phosphate loses 18 kilograms of water of crystallization as vapour: such an amount will be found calorimetrically.

The verification may be carried out somewhat differently, since the heat evolved in the combination of water vapour to form water of crystallization may be divided into two parts, one (*L*) evolved on simple condensation of water, the other (*Q*) on combination of the water with the salt.

The latter may be found directly, since *L*, the latent heat of evaporation of water, is connected with its vapour pressure *P* by

$$\frac{d \log P}{dT} = \frac{L}{2T^2};$$

therefore

$$\frac{d \log P}{dT} - \frac{d \log p}{dT} = \frac{d \log \left( \frac{P}{p} \right)}{dT} = \frac{d \log F}{dT} = \frac{L - q}{2T^2} = \frac{Q}{2T^2},$$

in which *F* is the ratio between the pressures of pure water and the water of crystallization. If the value of *Q* for  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  be calculated, by integration, from two measurements according to the equation

$$\log \left( \frac{P_1}{P_2} \right) = \frac{Q}{2} \left( \frac{1}{T_2} - \frac{1}{T_1} \right),$$



then we have

Temp.	F	Q
18.25°	0.1905	3800
43.45°	0.3204	

whilst 3830 has been found for the difference between the heats of solution of the hydrated and anhydrous salt for 18 kilograms of water of crystallization.

## 2. Sudden Change of Maximum Pressure.

### *Preparation of Hydrates.*

If a hydrated salt be systematically deprived of water, and the vapour pressure continuously registered, the latter may be found constant, so long as sufficient water of crystallization is left to supply the pressure in question, by its evaporation. But the case is different when the withdrawal of water is accompanied by the formation of lower hydrates, as with copper sulphate<sup>1</sup>. The following data were obtained by gradual withdrawal of water (at 50°):—

$\text{CuSO}_4 \cdot 4\frac{1}{2} \text{H}_2\text{O}$	. . . .	46.3 mm.
$\text{CuSO}_4 \cdot 3\frac{1}{2} \text{H}_2\text{O}$	. . . .	47.1 "
$\text{CuSO}_4 \cdot 2\frac{1}{2} \text{H}_2\text{O}$	. . . .	29.9 "
$\text{CuSO}_4 \cdot 1\frac{1}{2} \text{H}_2\text{O}$	. . . .	29.7 "
$\text{CuSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$	. . . .	4.4 "

The general result is shown in Fig. 24, the pressures being drawn vertically, and the  $\text{CuSO}_4$  content towards the right: it appears that for compositions between  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  the pressure remains at 47 mm., then sinks to 30 mm., till only one molecule of water is left, forming  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ ; then the pressure falls to 4.4 mm., finally becoming zero for the anhydride. The sudden changes caused by the successive formation of the hydrates  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  offer a method for the discovery of all the hydrates existing at a given temperature; and since, in general, the loss of water is more rapid the greater the vapour pressure, we may, with Müller-Erbach, seek for such hydrates by systematically measuring

<sup>1</sup> Pareau, *Pompharometer*. Diss. 1875.

the rate of evaporation in a desiccator, only the gradual change of surface due to evaporation is a source of error.

Returning to copper sulphate, if we take the influence of temperature into account, and represent all the vapour pressures graphically in Fig. 24, we get three curves, 05,

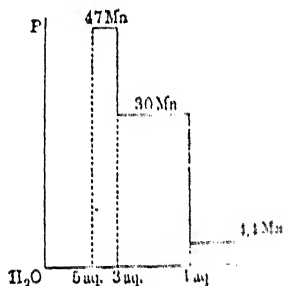


FIG. 24.

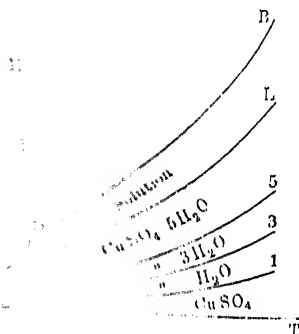
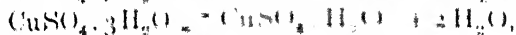
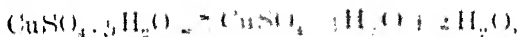


FIG. 25.

03, 01, relating to the hydrates  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ , and  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  respectively, and which consequently give the maximum pressures obtaining in the following states of equilibrium:—



The pressure diagram (Fig. 24) may be extended if we answer the question: What happens when the pressure of water vapour is increased beyond the maximum pressure for  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ? Saturated solution forms, as soon as the pressure begins to exceed the maximum for that solution; the latter—the vapour pressure of saturated copper sulphate solution—may be represented by AL, after which, by gradual increase of the pressure of the water vapour and dilution of the salt solution, we reach the limiting pressure—the saturation pressure for pure water—shown by the curve BD. Of the latter it may be remarked that it is cut at D—at  $0^\circ$ —by the corresponding curve for the maximum vapour

pressure of ice OD, and that the intersection A of the new curve with that of the saturated solution AL is the cryohydric point. The complex of lines BDOT consequently shows all the possibilities due to presence of water vapour, thus:

OD, pure ice; DB, pure water; D, the triple point.

BDAL, region of dilute solutions.

AL, saturated solution ending in the cryohydric point where vapour, ice, salt, and solution can coexist, and which is consequently a quadruple point.

LAO5, region of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

o5, simultaneous existence of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ .

5o3, region of  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ .

o3, simultaneous existence of  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ .

3o1, region of  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ .

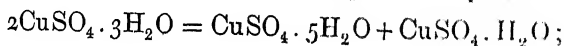
o1, simultaneous existence of  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  and  $\text{CuSO}_4$ .

1oT, region of  $\text{CuSO}_4$ .

Applying these results, AL is the limit of vapour pressure above which copper sulphate deliquesces, o5 that under which it effloresces, LAO5 the condition, as regards damp and dryness, which must be maintained in a dessicator—e. g. by dilute sulphuric acid—to obtain salt of the correct composition  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  from a preparation that is either damp or effloresced.

### 3. *Presence or Absence of Intermediate Hydrates.*

If we follow the previous diagram out towards the right, it may happen that two of the lines cut. Thus if the pressure o3 of  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  rises faster than o5 that of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , the two lines may cut, as at A (Fig. 26). The necessary consequence is plain: the salt with  $3\text{H}_2\text{O}$  comes to have a higher vapour pressure than that with  $5\text{H}_2\text{O}$ , and will change into the latter, according to the equation



in other words, the region of existence of  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  ceases, as the figure shows, at A, i.e. does not extend to temperatures above A<sup>1</sup>. In such facts we may find a reason for the non-existence of some possible hydrates:  $\text{CuSO}_4 \cdot 4\text{H}_2\text{O}$  may perhaps have a higher vapour pressure than  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , and consequently be impossible to prepare.

#### 4. *Phenomena of Melting in Aqueous Salts.* *Supersaturated Solutions.*

A second possibility, similar to that just discussed, is the intersection, not of the curves of two hydrates, but of the highest hydrate (5 in Fig. 25) with the saturation curve (AL in Fig. 25). For the same reason as in the preceding case the hydrate will, under these circumstances, break up, forming a lower hydrate, and the saturated solution, i.e. partial fusion, will occur. The best investigated case of this kind is that of Glauber salt.

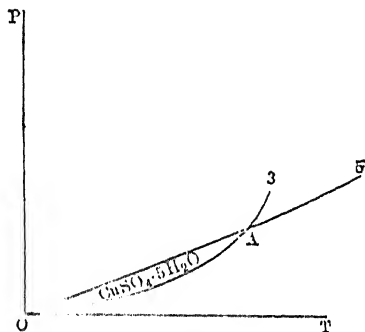
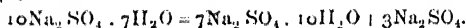


FIG. 26.

The salt in question,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , fuses at  $32.6^\circ$ , forming a saturated solution, with separation of  $\text{Na}_2\text{SO}_4$ . That the relations of pressure are actually those explained above has been shown by the pressure gauge of Fig. 23 used as a differential pressure gauge, containing on the one side dried Glauber salt (deprived of about half a molecule of water), and on the other damp salt. The difference of level in millimetres of oil, read off the scale, shows an

<sup>1</sup> There is evidence of such behaviour on the part of  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ , which separates out from supersaturated solutions of Glauber salt: it becomes turbid, gradually, until it is quite porcelain-white, in consequence of the change:



excess of pressure in favour of the saturated solution, at ordinary temperatures, which gradually falls off, and vanishes at  $32.6^{\circ}$ .

Temperature	$29^{\circ}$	$30.83^{\circ}$	$31.79^{\circ}$	$32.09^{\circ}$	$32.35^{\circ}$	$32.5^{\circ}$	$32.6^{\circ}$	$33.05^{\circ}$
Diff. of pressure	23.8	10.8	5.6	3.6	1.6	!	0	0

This transition at  $32.6^{\circ}$  is necessarily accompanied by a peculiarity in curve of solubility for Glauber salt, which may be deduced from the pressures of the saturated solutions. The change of pressure is known to be connected with the temperature by the equation

$$\frac{d \log p}{dT} = \frac{q}{2T^2},$$

where  $q$  is the heat evolved when 18 kilograms of water vapour condense to form saturated solution. This quantity

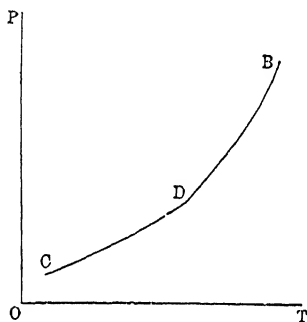


FIG. 27.

is obviously composed of two parts, that evolved on condensation, and that evolved when the condensed water is saturated. The first of these quantities is positive, according to Regnault 18 (606.5—0.695  $t$ ), the second in general negative. It is the latter that, on the transformation of Glauber salt at  $32.6^{\circ}$ , is suddenly altered by the latent

heat of fusion. It was  $-960$  and becomes  $+270$ , whence  $q$  before and after the transformation is respectively  $10510 - 960 = 9550$  and  $10780$ . Hence on passing the transition temperatures  $dP$  must suddenly increase; the corresponding curve shows a bend, as in Fig. 27. This bend must have its counterpart in the solubility curve; since the solution of the salt causes a diminution of pressure, sudden rise in the rate of increase of the pressure is necessarily accompanied by sudden fall in the rate of increase of the concentration, as shown in Fig. 28. This answers to the

measurements of solubility, as appears from the following numbers on the amount of  $\text{Na}_2\text{SO}_4$  which 100 parts of water can take up:—

Saturation with  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ :

31.84°	40	$\frac{dC}{dt} = \frac{9.78}{0.81} = 12.1.$
32.65°	49.78	

Saturation with  $\text{Na}_2\text{SO}_4$ :

32.65°	49.78	$\frac{dC}{dt} = \frac{-2.78}{17.35} = -0.16.$
50°	47	

It may be remarked further that this connexion may be made use of to draw a conclusion in the reverse order. In fact, it may be stated generally that if a salt suffers a transformation at a definite temperature, the solubility of the product of transformation must, above that temperature, be less than that of the original salt, since only in that case will the transformation be effected by contact with a trace of the solvent. Thus, once for all, the

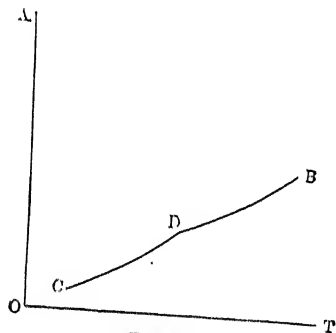


FIG. 28.

necessity is shown of a downward bend in the curve of solubility at the transition temperature. From this follows the necessity of an upward bend in the curve of vapour pressure, and, to go further, of an absorption of heat in the transformation that is brought about by rise of temperature.

The bend in the solubility curve which is thus genetically connected with the phenomenon of transformation, with absorption of heat, stands also in a near relation with the existence of supersaturated solutions. If the line BD in Fig. 28 be produced to the left as DE, the area lying between DE and DC is the graphical representation of solutions which

possess the double character of being supersaturated with respect to  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and unsaturated with respect to  $\text{Na}_2\text{SO}_4$ ; this area expresses, therefore, the long known supersaturated Glauber salt solutions. It is worth notice that this reasoning indicates the existence of a second class of supersaturated solutions; if  $\text{CD}$  be produced to the right as  $\text{DF}$ , the area between  $\text{DF}$  and  $\text{DB}$  expresses supersaturation with respect to  $\text{Na}_2\text{SO}_4$  and unsaturation with respect to  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . These supersaturated solutions of the second kind seem, however, to be less stable. It must be remarked in conclusion that such a pair of supersaturated solutions may be associated not only with the existence of two hydrates, such as Glauber salt, soda, &c., but with any transformation, e.g. of ammonium nitrate, in which only the crystalline form changes.

Finally, let us complete the consideration of Glauber salt by taking account of the peculiar hydrate with seven

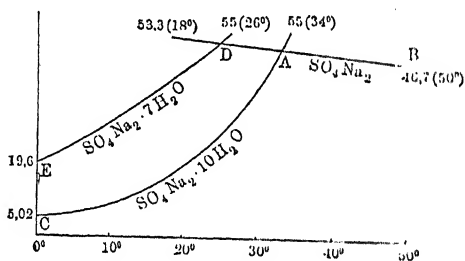


FIG. 29.

molecules of water of crystallization that separates, as large transparent crystals, from supersaturated solutions in the cold. Löwel determined the solubility of this salt, which is given by  $\text{ED}$  in Fig. 29, whilst  $\text{CA}$  is that of Glauber salt, measured up to  $34^\circ$ , and  $\text{BD}$  that of the anhydrous salt, measured down to  $18^\circ$ . It appears that all saturated solutions of the heptahydrate are supersaturated, whilst for Glauber salt and the anhydride that is only the case for certain temperatures. The chief

point is the vapour pressure of the third salt,  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ , which cannot be directly measured, but is necessarily greater than that of Glauber salt,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , although the latter contains more water. Let us then assume the pressures corresponding to Fig. 29 and insert them in Fig. 30.

The pressure of the saturated anhydride solution is shown by DA, A being the point  $32.6^\circ$  at which Glauber salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) melts, with formation of the anhydride solution, and at which therefore its pressure becomes equal to that (30.82 mm.) of the solution, to exceed it afterwards; Glauber salt is therefore represented by the curve  $10\text{H}_2\text{O}$ . At D, temperature  $24.2^\circ$  according to the measurements of solubility as shown by Fig. 29, a similar fusion of  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  must take place: that salt accordingly must, at that temperature, equal in vapour pressure the solution of the anhydride. It is represented in Fig. 30 by  $7\text{H}_2\text{O}$ , and obviously exceeds Glauber salt in pressure. Hence the peculiar change which gradually converts the heptahydrate into a porcelain-white mass, and apparently consists

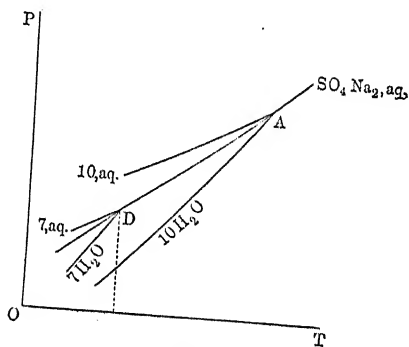


Fig. 30.

in decomposition into decahydrate and anhydride. For the sake of completeness the pressures of the saturated solutions of heptahydrate and decahydrate are shown in Fig. 30 by the lines 7aq and 10aq. They meet that of the anhydride solution in D and A on account of equality of solubility, and to the left of those points lie higher, on account of their lower concentration.



5. *Complete Fusion of a Hydrate and the Existence of Two Saturated Solutions at the same Temperature.*

The last point to consider with regard to hydrates is the fact that some hydrates melt, but, unlike Glauber salt, which gives rise to a lower hydrate, form a clear liquid. Roozeboom<sup>1</sup> has studied the phenomenon thoroughly in the case of calcium chloride,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . It is well known that this salt melts at  $30.2^\circ$ , so that the solubility curve may be followed to that point, and gives from the cryohyric point ( $-55^\circ$ ) the following results:—

Temperature.	Composition of the Solution.
$-55^\circ$ . . .	$\text{CaCl}_2 \cdot 14.5 \text{ H}_2\text{O}$
$0^\circ$ . . .	„ 10.37 „
$10^\circ$ . . .	„ 9.49 „
$20^\circ$ . . .	„ 8.28 „
$25^\circ$ . . .	„ 7.52 „
$28.5^\circ$ . . .	„ 6.81 „
$29.5^\circ$ . . .	„ 6.46 „
$30.2^\circ$ . . .	„ 6 „

The peculiarity of this and similar cases lies in the existence of saturated solutions that are richer in  $\text{CaCl}_2$  and yet can be kept at a lower temperature, i. e. below  $30.2^\circ$ . This becomes plain if one starts from  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , melting at  $30.2^\circ$ , and bears in mind that this melting point, like any other, is lowered by addition of foreign substances, e. g. by addition of water or of calcium chloride; in the first case the preceding solubility curve is obtained, in the second a new one to which the following observations refer:—

$29.6^\circ$ . . .	$\text{CaCl}_2 \cdot 5.7 \text{ H}_2\text{O}$ ,
$29.2^\circ$ . . .	$\text{CaCl}_2 \cdot 5.41 \text{ H}_2\text{O}$ .

This lowering of the melting point may be derived from the usual formula for the molecular depression ( $t$ ):—

$$t = \frac{0.02 T^2}{W} = 35.3, \quad T = 273 + 30.2, \quad W = 52.1^2,$$

provided the hydrate melts without decomposition, as is the case with the hydrate of phosphorus pentoxide, i. e. phos-

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 4. 31.

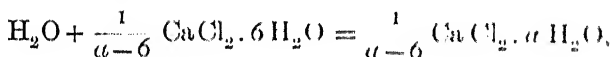
<sup>2</sup> Pickering, *Berl. Ber.* 27. 74.

phoric acid, and more definitely still with the so-called carbohydrates. If, however, decomposition occurs on melting, and consequently equilibrium between water and a lower hydrate, the added molecule of water will not produce the calculated molecular depression, because, amongst other things, part of the added water disappears in consequence of the displacement of equilibrium<sup>1</sup>.

A very comprehensive view of these phenomena can be arrived at from the vapour pressures of the saturated solutions. Taking the well-known formula

$$\frac{d \log P}{dT} = \frac{q}{2T^2},$$

in the case of a saturated solution of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  the value of  $q$  is the sum of the latent heat of evaporation  $L$  of 18 kilograms of water and of the heat (here negative) which is developed on saturation of those 18 kilograms with  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  according to the equation



in which  $\text{CaCl}_2 \cdot a\text{H}_2\text{O}$  gives the composition of the saturated solution. If  $-W$  is the heat evolved on solution of the molecular quantity of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  to saturation then

$$q = L - \frac{W}{a-6}.$$

$q$  has its maximum value when the solubility is least, i.e.  $a$  is greatest, or at the cryohydric point ( $a = 14.5$ ).  $q$  then falls till for

$$L = \frac{W}{a-6}$$

it becomes zero, and afterwards negative till it reaches  $-\infty$  for  $a = 6$ , and for  $a < 6$  recovers a positive value.

These changes in  $q$  correspond as regards pressure to an increase up to a maximum (at  $28.5^\circ$ , according to p. 41), then a fall, and at the melting point  $35.2^\circ$ , where  $a = 6$ ,

<sup>1</sup> Stortenbeker, *Zeitschr. f. Phys. Chem.* 10, 201; Le Châtelier, *l.c.* 21, 255.



Let us consider now the relation between pressure and concentration, which may be represented in Fig. 31 under OT, the quantity of  $\text{CaCl}_2$  in 100 parts of solution being measured along O100. A corresponds to the concentration at the cryohydric point, AD to the freezing points of all solutions of calcium chloride, as far as the freezing point of pure water at D. From A in the other direction proceeds the solubility curve for  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  in two parts corresponding to  $\text{A}_1\text{F}_1$  and  $\text{F}_1\text{H}_1$ , and referring to solutions containing more and less water respectively than the hydrate. The connexion between concentration and vapour pressure gives indications of the course of these two branches, especially at F where they meet. The increase of pressure with temperature  $\frac{dP}{dT}$  is, on the one hand, a result of the influence of temperature apart from change of concentration  $(\frac{\partial P}{\partial T})_c$ , on the other due to the accompanying change of concentration  $\frac{dC}{dT}$  or

$$\frac{dP}{dT} = \left(\frac{\partial P}{\partial T}\right)_c + \frac{dC}{dT} \left(\frac{\partial P}{\partial C}\right)_T,$$

in which  $(\frac{\partial P}{\partial C})_T$  is the increase of pressure accompanying increase of concentration, a quantity known to be negative, say  $-a$ . Hence

$$\frac{dC}{dT} = \frac{\left(\frac{\partial P}{\partial T}\right)_c - \frac{dP}{dT}}{a} = \frac{P(q_0 - q)}{2aT^2};$$

wherein  $q_0$  is the heat developed when 18 kilograms of water condense to form saturated solution, as by mixture with an infinite quantity of the latter;  $q$  is the heat given out on saturation of 18 kilograms of water with  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . The latter is at the melting point negatively infinite, so that  $\frac{dC}{dT}$  is positively infinite, i.e. the saturation curve has a vertical tangent at F as shown in

Fig. 31. This is in harmony with the expectation on p. 69 above, that the lowering of the melting point of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  by addition of  $\text{CaCl}_2$  or  $\text{H}_2\text{O}$  is less than normal.

In completion it may be remarked that we have arrived in two different ways at the conclusion that the lowering of the melting point of hydrated calcium chloride by addition of water or calcium chloride is less than normal. Both arguments proceed essentially from the same fundamental assumption; the first from the partial dissociation of the hydrate for equilibrium in the fused state; the second on the existence of a pressure of water vapour for the fused hydrate, which is intimately bound up with the partial dissociation of the hydrate. Hydrates, therefore, that when melted have no vapour pressure of water<sup>1</sup>, must give the normal lowering of melting point on addition of either component; that is very approximately the case for bodies like sulphuric acid, and completely so for the carbohydrates.

#### 6. *Review of the Complete Relations of Two Bodies which act chemically on one another. Chlorine and Iodine.*

Now that the leading phenomena shown by two bodies that act chemically on one another have been discussed, it is desirable to explain the complete relations in some special instance, i.e. to define what occurs when, under varying temperature, pressure, and mass-ratio, two chemical re-agents are placed in contact. The mutual behaviour of chlorine and iodine will be chosen as example<sup>2</sup>.

The complete solution of the problem is, then, to determine in all possible cases what occurs to a given mass of chlorine when it is placed in contact with a given mass of iodine, at determinate pressure and temperature. The problem has only been partially solved, since with regard

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 10. 201.

<sup>2</sup> Stortenbeker, *L. c.* 3. 11.

to pressure only those possible cases have been investigated in which formation of vapour occurs, and consequently the pressure is the maximum vapour pressure.

We will develop the complete picture, obtained subject to that reservation, starting from the well-known solid monochloride of iodine  $\text{ICl}$ . It melts at  $27.2^\circ$ , and accordingly its melting point and composition are represented in Fig. 32; ratios of the number of atoms are measured verti-

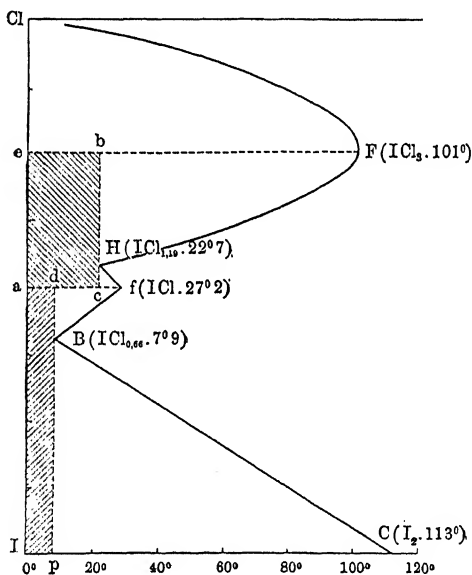


FIG. 32.

cally, so that the point in question lies halfway between the two horizontal lines which represent pure chlorine and iodine, and at a distance towards the right corresponding to  $27.2^\circ$ . That point  $f$  plays the same part as the melting point of hydrated calcium chloride, and from it also two branches proceed relating to the addition of chlorine and iodine respectively. Beginning with addition of iodine, the series of lower melting points produced constitute the line  $fB$ . This line follows the equation

$$t = \frac{0.02T^2}{W} (T = 273 + 27.2^\circ : W = 16.42);$$

which shows that, unlike hydrated calcium chloride, the added iodine acts as a foreign substance, and that iodine chloride suffers no appreciable dissociation on melting, which is in accordance with the observation that its vapour consists essentially of chlorine and iodine in combination. The line  $fB$  stops on saturation with iodine, when the melting point has fallen to  $7.9^\circ$ , and the composition of the mixture may be expressed by  $ICl_{0.66}$ .

The liquid then freezes on cooling, or rather on withdrawal of heat, to a mixture of iodine and iodine chloride, while the temperature remains at  $7.9^\circ$  until the whole is solidified. The point  $B$  is, however, also on the line of melting points for iodine, which extends, on gradual addition of chlorine or iodine chloride to iodine, from  $113^\circ$ , the melting point of pure iodine, to  $7.9^\circ$ , the melting point on saturation with iodine chloride. This line is marked  $BC$ , and completes the diagram of what is obtainable, starting from iodine chloride, by addition of iodine.

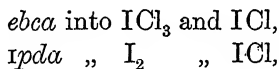
Starting again from iodine chloride, i.e. from  $f$ , another line is obtained by addition of chlorine, which represents the lowering of the melting point of iodine chloride by excess of chlorine— $fH$ —terminating in  $H$  at  $22.7^\circ$  on saturation with iodine trichloride; the liquid there has the composition  $ICl_{1.19}$  and freezes on withdrawal of heat completely to a mixture of  $ICl$  and  $ICl_3$ , the temperature remaining constant at  $22.7^\circ$ . At  $H$  is met the curve expressing lowering of the melting point of  $ICl_3$  on addition of iodine or monochloride of iodine, and starting from  $F$  at  $101^\circ$ , the melting point of pure iodine trichloride. The graphical representation is completed by the curve, also starting from  $F$ , for the lowering of the melting point of  $ICl_3$  by addition of chlorine. The investigation has not been carried out completely in this direction. The result will depend on the form in which the chlorine separates on continually greater fall of temperature and increase of chlorine content. If

that takes place in the solid state the figure ends above, as it does below with iodine, in the melting-point curve of chlorine; the latter begins at some point of the curve to the left above *F*, with simultaneous presence of solid  $\text{Cl}_2$  and  $\text{ICl}_3$ ; and runs to the right upwards, to meet the chlorine axis at the melting point of pure chlorine. Since that melting point is  $-102^\circ$  the branch in question is omitted from Fig. 32.

Now that the entire group of relations has been explained with the aid of Fig. 32, let us again divide the diagram into areas and describe the physical meaning of each.

To the right of the broken line  $\text{ClFhfBC}$  we are concerned with liquid mixtures, whose composition may vary continuously from pure chlorine to pure iodine; the pressure being the maximum vapour pressure. The broken line is the boundary at which a solid separates from the liquid mixture; along  $\text{ClfF}$  iodine trichloride, along  $\text{hfB}$  iodine monochloride, and along  $\text{BC}$  iodine.

To the left of the broken line we have states which are not stable and decompose into two components, either into two solids:



or into solid and solution:

$\text{Clfe}$  and  $\text{HFfb}$  into  $\text{ICl}_3$  and the solutions represented by  $\text{Clf}$  and  $\text{fF}$  respectively;

$\text{Hfc}$  and  $\text{Bfd}$  into  $\text{ICl}$  and the solutions represented by  $\text{hf}$  and  $\text{fB}$  respectively;

$\text{BCp}$  into  $\text{I}_2$  and the solution represented by  $\text{BC}$ .

Only the horizontal lines through  $\text{Cl}$ ,  $\text{F}$ ,  $\text{f}$ , and  $\text{c}$  correspond to single substances, viz. chlorine, trichloride, monochloride, and iodine.

The following points may be noted with regard to the number of phases present:—

1. The area to the right of the broken curve implies two—liquid and vapour.



2. The curve itself implies three, since a solid substance separates there.

3. The first point of intersection of two branches of the broken curve implies four, since the substances represented by each of the two branches may be present.

Looked at from this point of view, H and B are quadruple points at which the following bodies are in equilibrium:—

At H: vapour, liquid  $\text{ICl}_{1.19}$ ,  $\text{ICl}_3$ ,  $\text{ICl}$ ;

At B: vapour, liquid  $\text{ICl}_{0.66}$ ,  $\text{I}_2$ ,  $\text{ICl}$ .

To complete the above we have now to take into account the vapour, which it was assumed is always present. In the hydrates previously considered this was simpler, since the vapour had only one component—water—so that a simple measurement of vapour pressure was enough.

In the present case it is different, since chlorine and iodine both exist in the vapour, and partly also combined: analysis as well as measurement of pressure is therefore necessary. Both results will be stated in order.

A notion of the pressure relations may be obtained by considering Fig. 33, which contains the leading results, in the light of the rules already discussed.

The leading data refer to the temperatures at which phenomena of melting occur, points expressed by the same letters as in Fig. 32:

$D_1$	melting point of $\text{Cl}_2(-102^\circ)$	pressure 11 atm.
$F_1$	" $\text{ICl}_3(101^\circ)$	" 16 "
$H_1$	" $\text{ICl}_3 \cdot \text{ICl}(22.7^\circ)$	" 42 mm.
$f_1$	" $\text{ICl}(27.2^\circ)$	" 37 "
$B_1$	" $\text{ICl} \cdot \text{I}_2(7.9^\circ)$	" 11 "
$C_1$	" $\text{I}_2(113^\circ)$	" 91 "

Now trichloride of iodine in the fused state is partially dissociated into chlorine and iodine monochloride, as is shown by the fact that the vapour in equilibrium with the liquid contains chlorine and a little of the monochloride. The pressure curve, of which  $F_1$  is a point, corresponds exactly to the pressure curve for hydrated calcium chloride given in Fig. 31 by  $A_1M_1F_1H_1$ ; there is a vertical tangent

at  $F_1$ , then the curve proceeds upwards and to the left of  $F_1$ , which refers to the lowering of the temperature due to increased chlorine content, and therefore at first an increase of

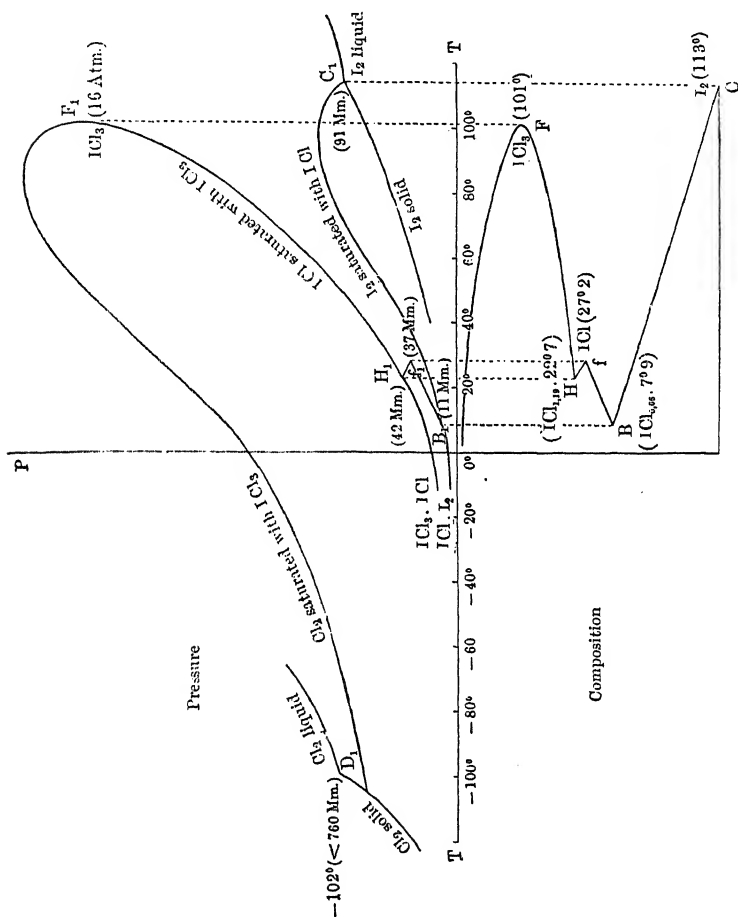


Fig. 33.

pressure; afterwards the pressure falls, and the curve meets that corresponding to the vapour pressure of solid chlorine,  $OA$  (Fig. 31). Thirdly, the branch  $F_1H_1$ , where with fall of temperature the proportion of chlorine falls off till, at  $H_1$ ,

ICl as well as  $\text{ICl}_3$  separates from the liquid. To the left of  $H_1$  the pressure curve for  $\text{ICl}_3$  appears, like that of the hexahydrate in the case of calcium chloride. The broken line  $H_1 f_1 B_1$ , that starts from  $H_1$  and refers to the melting point of  $\text{ICl}$  ( $f_1$ ) and its lowering by addition of  $\text{ICl}_3$  ( $f_H$ ) and of  $\text{I}_2$  ( $f_B$ ), would correspond exactly to the line through  $F_1$  if  $\text{ICl}$  broke up on melting. Since that is not the case the existence of a vertical tangent is doubtful, and there are rather two distinct alterations of pressure caused by solution of  $\text{ICl}_3$  and of  $\text{I}_2$  in the  $\text{ICl}$ . To the left of  $B_1$  the pressure curve of  $\text{ICl}$  reappears. The last branch  $B_1 C_1$  refers to saturation of liquid iodine with  $\text{ICl}$  on rise of temperature: it ends with a vertical tangent at the melting point of iodine, where also the pressure curves for solid and liquid iodine meet.

### E. Physical Equilibrium of Three Substances.

If three different substances are to be dealt with, and, chemical action being excluded, the possibilities of mutual solution, &c., are to be considered, the problem is an extensive one, and its scope and partial solution may best be given by means of a definite example.

The example is taken from the researches of Wright<sup>1</sup> on alloys of three metals, which were thus essentially devoted to the behaviour of mixtures of three metals. Another case is that of three liquids, acetic acid, chloroform, and water, and the equilibrium conditions here too, being easily followed, will be considered in some detail. The case is most simply studied by starting from the almost immiscible pair chloroform-water, and following out the influence which gradual addition of acetic acid exercises. Gradually increasing mutual solubility is then developed, like that produced by rise of temperature. The following numbers indicate the fact:—

<sup>1</sup> *Proc. Roy. Soc.* 49. 174, 50. 372.

Composition of the two layers on gradual addition of acetic acid at 18°:

No.	Heavy layer.			Light layer.		
	CHCl <sub>3</sub>	H <sub>2</sub> O	CH <sub>3</sub> COOH	CHCl <sub>3</sub>	H <sub>2</sub> O	CH <sub>3</sub> COOH
1	67	5	28	18	31	51
2	60	8	32	25	25	50
3	56	10	34	29	23	48

This increase of mutual solubility ends, as when it is produced by rise of temperature, in complete miscibility, which occurs at the composition:



The graphical representation of these relations may be accomplished by means of an equilateral triangle ABC, the weight of the components present being supposed distributed between the angular points, e. g. CHCl<sub>3</sub>, i. e. 42, at A; H<sub>2</sub>O,

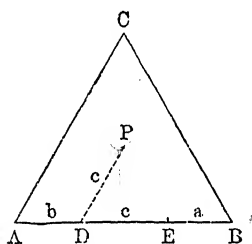


FIG. 34.

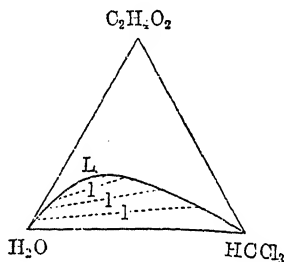


FIG. 35.

i. e. 16, at B; and C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>, i. e. 42, at C. The centre of gravity L of this system of weights may thus be taken to represent the composition in question. The lines drawn from that point at right angles to BC, AC, and AB, whose sum is constant, will show the quantities of the three components, respectively.

The representation gains considerably in clearness by making use of the equilateral triangle in another way<sup>1</sup>, one of the edges—say AB (Fig. 34)—being divided into three parts, AD, DE, EB, proportional to the quantities *b*, *c*, *a* of the substances B, C, A. If now DP be drawn from D of length

<sup>1</sup> Löwenherz, *Zeitschr. f. Phys. Chem.* 13. 464; Roozeboom, l. c. 15. 147.

equal to  $c$  and parallel to  $AC$ , the point  $P$  expresses simply the composition required.  $AD$  is the quantity of the substance  $B$ ,  $DP$  that of  $C$ , and length of side minus those two lengths gives the quantity of  $A$ .

If this method be applied to the case mentioned, and water, chloroform, and acetic acid be supposed at  $A$ ,  $B$ , and  $C$  respectively, Fig. 35 represents the phenomena. The curve, ending at  $H_2O$  and  $CHCl_3$ , shows the gradual union of the two layers resulting from addition of acetic acid. The auxiliary lines  $l$  join the pairs of mixtures which are in equilibrium with one another, and their limit  $L$  shows the composition at which complete miscibility occurs.

In conclusion it may be remarked that the above mode of representation is quite in place in dealing with three bodies that are practically equal in position. If, as mostly happens, two of the bodies behave quite differently to the third, e.g. two salts and water, of which the salts only dissolve in the third substance, as indeed is more or less true in the preceding case, the use of rectangular axes is to be preferred. The quantity of the two bodies may then be expressed in any convenient way, such as by reference to a fixed mass of the third, and represented by ordinates or abscissae in the usual way.

*Influence of Temperature.* After choosing one of the above modes of representation, the temperature may be introduced, most conveniently for graphical purposes, by measuring it along an axis at right angles to the plane on which the diagram of composition is drawn, and through the origin ( $A$ , Fig. 34). On rise of temperature the diagram changes in a simple manner, since, through gradual increase of solubility, complete mixture is reached, when the entire triangle represents a homogeneous fluid. On fall of temperature the phenomena grow more complex, till the gradual solidification of the three substances restores simplicity, and in general complete absence of mixture causes the problem to disappear.

## F. Chemical Equilibrium between Three Substances.

The investigation of chemical equilibrium also, when the mutual action of three bodies is involved, has only been carried out systematically in a few cases. The most importance is to be attached to double salts, of which we will take schönite as an example, and on the other hand explain the more complicated relations of the double compounds of ferric chloride and hydrochloric acid.

### 1. *Schönite*, $K_2Mg(SO_4)_2 \cdot 6H_2O$ <sup>1</sup>.

The investigation of this double salt, whose existence in contact with solution is limited by two transformations at  $-3^\circ$  and  $+92^\circ$  respectively, had for object to find quite generally the possibilities of its occurrence. The investigation shows what happens to a mixture of  $K_2SO_4$ ,  $MgSO_4$ , and  $H_2O$ , when the proportion and the temperature are changed. The only restriction in the circumstances was with regard to pressure, which was always the saturation pressure of the solution, so that the relations are those which are observed in working with open vessels. The temperature, on the other hand, extended to formation of ice, or to cryohydric phenomena, at which the relations of equilibrium naturally cease, and upwards to the boiling point of the solutions in question.

*The two transformations of schönite.* The two transformations which limit the region of existence of schönite are not of the same kind. On cooling in contact with water, schönite takes up the latter at a certain temperature, and breaks up into its component salts. On heating, also, to a definite temperature it loses water, but without further decomposition, forming a less hydrated double salt,  $K_2Mg(SO_4)_2 \cdot 4H_2O$ , which, by comparison with astrakanite,  $Na_2Mg(SO_4)_2 \cdot 4H_2O$ , of similar composition, may be called

<sup>1</sup> Van der Heide, *Zeitschr. f. Phys. Chem.* 12. 416.

equal to  $c$  and parallel to  $AC$ , the point  $P$  expresses simply the composition required.  $AD$  is the quantity of the substance  $B$ ,  $DP$  that of  $C$ , and length of side minus those two lengths gives the quantity of  $A$ .

If this method be applied to the case mentioned, and water, chloroform, and acetic acid be supposed at  $A$ ,  $B$ , and  $C$  respectively, Fig. 35 represents the phenomena. The curve, ending at  $H_2O$  and  $CHCl_3$ , shows the gradual union of the two layers resulting from addition of acetic acid. The auxiliary lines  $l$  join the pairs of mixtures which are in equilibrium with one another, and their limit  $L$  shows the composition at which complete miscibility occurs.

In conclusion it may be remarked that the above mode of representation is quite in place in dealing with three bodies that are practically equal in position. If, as mostly happens, two of the bodies behave quite differently to the third, e. g. two salts and water, of which the salts only dissolve in the third substance, as indeed is more or less true in the preceding case, the use of rectangular axes is to be preferred. The quantity of the two bodies may then be expressed in any convenient way, such as by reference to a fixed mass of the third, and represented by ordinates or abscissae in the usual way.

*Influence of Temperature.* After choosing one of the above modes of representation, the temperature may be introduced, most conveniently for graphical purposes, by measuring it along an axis at right angles to the plane on which the diagram of composition is drawn, and through the origin ( $A$ , Fig. 34). On rise of temperature the diagram changes in a simple manner, since, through gradual increase of solubility, complete mixture is reached, when the entire triangle represents a homogeneous fluid. On fall of temperature the phenomena grow more complex, till the gradual solidification of the three substances restores simplicity, and in general complete absence of mixture causes the problem

## F. Chemical Equilibrium between Three Substances.

The investigation of chemical equilibrium also, when the mutual action of three bodies is involved, has only been carried out systematically in a few cases. The most importance is to be attached to double salts, of which we will take schönite as an example, and on the other hand explain the more complicated relations of the double compounds of ferric chloride and hydrochloric acid.

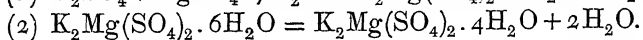
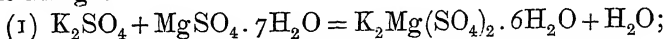
### 1. *Schönite*, $K_2Mg(SO_4)_2 \cdot 6H_2O$ <sup>1</sup>.

The investigation of this double salt, whose existence in contact with solution is limited by two transformations at  $-3^\circ$  and  $+92^\circ$  respectively, had for object to find quite generally the possibilities of its occurrence. The investigation shows what happens to a mixture of  $K_2SO_4$ ,  $MgSO_4$ , and  $H_2O$ , when the proportion and the temperature are changed. The only restriction in the circumstances was with regard to pressure, which was always the saturation pressure of the solution, so that the relations are those which are observed in working with open vessels. The temperature, on the other hand, extended to formation of ice, or to cryohydric phenomena, at which the relations of equilibrium naturally cease, and upwards to the boiling point of the solutions in question.

*The two transformations of schönite.* The two transformations which limit the region of existence of schönite are not of the same kind. On cooling in contact with water, schönite takes up the latter at a certain temperature, and breaks up into its component salts. On heating, also, to a definite temperature it loses water, but without further decomposition, forming a less hydrated double salt,  $K_2Mg(SO_4)_2 \cdot 4H_2O$ , which, by comparison with astrakanite,  $Na_2Mg(SO_4)_2 \cdot 4H_2O$ , of which it is isomorphous, is



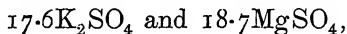
potassium-astrakanite<sup>1</sup>. The following equations express the changes:—



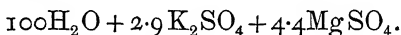
The first transformation was apparent when, on crystallization of a solution of the two sulphates in water overnight in winter, the whole mass became solid, partly consisting of ice, which on thawing out gave crystals of potassium and magnesium sulphates side by side, schönite being absent; but, on slow rise to atmospheric temperature, appeared with absorption of the other salts. To find the exact temperature boundary in this case, instead of the dilatometric method referred to previously, a thermometric method, more convenient for low temperatures, was used. About 80 grams of schönite and 40 grams of water were mixed, and whilst stirred with a thermometer, cooled in salt and snow: the fall of temperature per minute was noted, and showed a minimum at  $-3^\circ$ . After the mass had become completely solid, it was surrounded with cotton wool, and left to itself, the rise of temperature being noted: again the thermometer rested at  $-3^\circ$ . This is the temperature at which the transformation (1) takes place. The second transformation was shown by the fact that, at high temperatures, solutions containing potassium and magnesium sulphates crystallized out into potassium-astrakanite,  $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , instead of schönite,  $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , and the dilatometer showed that the change occurs at  $92^\circ$ . In contact with water, then, the extreme limits for the existence of schönite are  $-3^\circ$  and  $+92^\circ$ .

*Survey of the general behaviour of magnesium sulphate, potassium sulphate, and water.* After noting the above data we may proceed to the more general question: What is produced when the two sulphates are brought, in any proportions, into water at any temperature? Still another temperature of transformation may be foreseen, deduced from a closer consideration of the decomposition of schönite

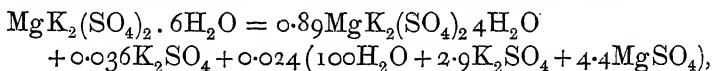
at  $92^\circ$ . Analysis of the saturated solution of the transformed schönite at  $92^\circ$  gave for 100 parts of solution :



i. e. in molecules



The exact formula of the transformation is therefore



i. e. separation of potassium sulphate occurs, but not of magnesium sulphate.

That, however, shows at the same time that there must be a second conversion temperature for schönite when it is in presence of excess of magnesium sulphate. The dilatometer filled with the two salts shows in fact the expected transformation at  $72^\circ$ . The dilatometer, however, shows yet another transformation at  $47.3^\circ$ , depending on a change of magnesium sulphate from the heptahydrate  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  into hexahydrate  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ .

With that the chief relations of schönite are made plain, and its conditions of existence may be represented by a diagram bounded by four transition-points, the exact form being determined by means of solubility measurements.

*Measurements of solubility.* The above determination at  $92^\circ$ , where simultaneous saturation with  $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{K}_2\text{SO}_4$  occurs, is represented on Figs. 36 and 37 in the way described previously, as the point H, by drawing  $\text{H}_1$ , the vertical projection for the  $\text{MgSO}_4$ , and  $\text{H}_2$ , the horizontal projection for the  $\text{K}_2\text{SO}_4$ , above and below the temperature axis respectively.

The second temperature,  $72^\circ$ , at which transformation of schönite in presence of hexahydric magnesium sulphate occurs, is a point of saturation for  $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ . The result of a measurement of solubility was for 100 parts of solution



The third transition point,  $47.3^\circ$ , at which conversion of the heptahydrate of magnesium sulphate to the hexa-

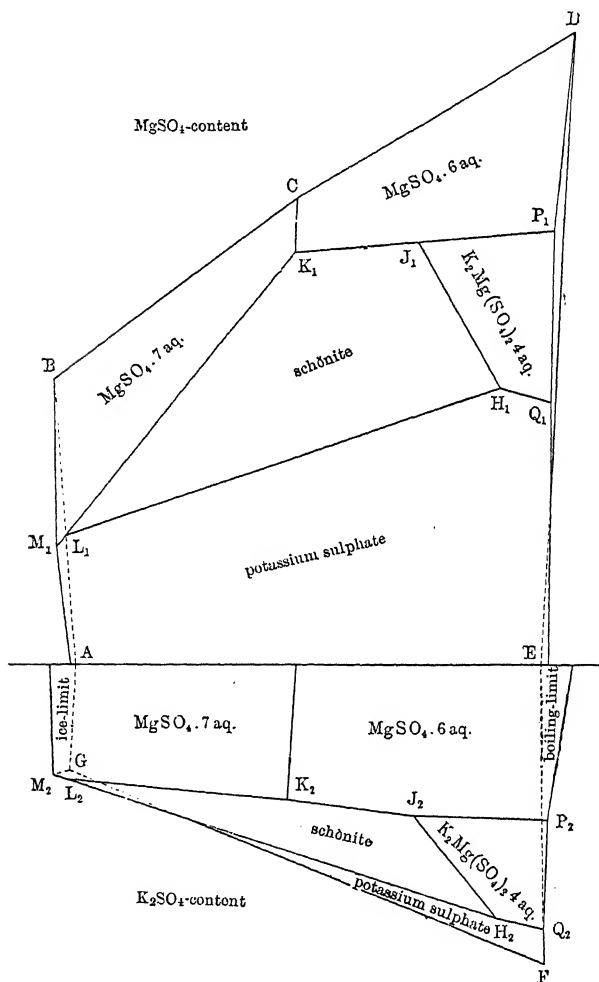


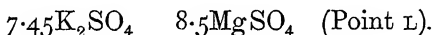
FIG. 36.

hydrate occurs in presence of schönite, and consequently

$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  occurs, gave as the result of the solubility measurement :



Finally, schönite decomposes into the separate sulphates at  $-3^\circ$ , so that their simultaneous saturation with  $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , and  $\text{K}_2\text{SO}_4$  is possible. Result :



The schönite diagram is therefore given by joining the points LKJH. Hence we have

H for saturation with $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , $\text{K}_2\text{SO}_4$					
HJ	"	"	"	"	—
J	"	"	"	"	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$
JK	"	"	"	"	—
K	"	"	"	"	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
KL	"	"	"	"	—
L	"	"	"	"	$\text{K}_2\text{SO}_4$
LH	"	"	"	"	—
HJKL	"	"	"	"	—

According to Etard<sup>1</sup>, the lines in question when, as here, the solubility is expressed for 100 parts of solution, go fairly straight; whilst the curves extending from  $-3^\circ$  to  $+92^\circ$  for saturation with schönite and with potassium sulphate are accurately given by the following observations of Precht and Wittgen<sup>2</sup> :—

Temp.	$\text{K}_2\text{SO}_4$	$\text{MgSO}_4$	Temp.	$\text{K}_2\text{SO}_4$	$\text{MgSO}_4$
$10^\circ$	9.4	9.8	$60^\circ$	15.2	16.3
$20^\circ$	10.9	10.8	$70^\circ$	15.6	16.8
$30^\circ$	12.4	11.8	$80^\circ$	16.0	17.1
$40^\circ$	13.8	13.1	$80^\circ$	16.6	18.1
$50^\circ$	14.7	14.8	$90^\circ$	17.2	18.2

*Surroundings of the schönite diagram.* After defining on all sides the boundary of the schönite area, we have to consider more in detail what areas are adjacent to it. Below LH (Fig. 37), which represents saturation with schönite and potassium sulphate, lies the area referring to saturation with potassium sulphate above, and that, by gradual diminution

<sup>1</sup> *Comptes Rend.* 98, 993, 1276, 1432.

<sup>2</sup> *Berl. Ber.* 15, 1671.

of the content in magnesium sulphate, passes into the line of solubility for pure potassium sulphate, GF on the horizontal plane of projection.

Above LKJ lies the area of saturation with magnesium sulphate, which passes into BD on the vertical plane, the line of saturation for that salt by itself. Only here we have to take account of the conversion of heptahydrate into hexahydrate, which for the pure salt takes place at  $48^\circ$  (point c). That point must therefore be joined to K by a line which represents saturation with both hydrates, and divides

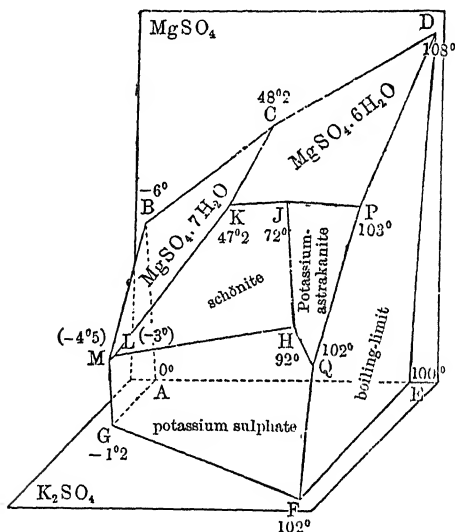


FIG. 37.

the magnesium sulphate area into two parts relating to the hepta- and hexa-hydrate.

The graphical representation may now be completed on all sides by means of the ice area on the left, and the boiling point limit on the right.

The ice-area is given by three observations :

1. Cryohydric temperature for magnesium sulphate,  $-6^\circ$  (Guthrie) marked p in the figure.

2. Cryohydric temperature for potassium sulphate,  $-1.2^{\circ}$ , marked *g* in the figure.

3. Cryohydric temperature for the mixed sulphates,  $-4.5^{\circ}$ .

The composition of the solution at the latter temperature may be calculated by an application of Meyerhoffer's rule, according to which, at a transition point, the solubility curve for the salt remaining untransformed suffers no special modification. The content of potassium sulphate of the solution saturated with both sulphates at  $-4.5^{\circ}$  is therefore given by producing the line for the  $K_2SO_4$  content on simultaneous saturation with  $K_2SO_4$  and  $K_2Mg(SO_4)_2 \cdot 6H_2O$  ( $H_2I_2$  in the horizontal projection). In the same way the content of  $MgSO_4$  is given by producing  $H_1L_1$  in the vertical projection, so that *M* represents the composition of the solution at the cryohydric point. The ice area is therefore an almost vertical plane through *B*, *M*, *+*, and *A* (freezing point of water), whose bounding lines and points have the following meaning:—

*A*, freezing point of pure water ( $0^{\circ}$ ).

*AB*, freezing point of magnesium sulphate solution.

*B*, cryohydric point of magnesium sulphate solution ( $-6^{\circ}$ ).

*AG*, freezing point of potassium sulphate solution.

*g*, cryohydric point of potassium sulphate solution ( $-1.2^{\circ}$ ).

*BM*, freezing point of solutions saturated with magnesium sulphate, with gradual increase of potassium sulphate content.

*M*, cryohydric point for magnesium and potassium sulphates ( $-4.5^{\circ}$ ).

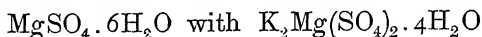
*GM*, freezing point of solutions saturated with potassium sulphate, with gradual increase of magnesium sulphate content, up to saturation with the latter also at *M*.

Finally, there is the steam area.

In the first place, we have to consider the boiling point of saturated magnesium sulphate on the vertical projection plane at *D* ( $108^{\circ}$ ), and that of saturated potassium sulphate on the horizontal plane at *F* ( $102$ ).

Secondly, the boiling point of pure water at E.

Between the two, magnesium and potassium sulphate, however, in consequence of the formation of potassium-astrakanite, we have the combinations

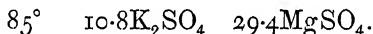


and  $\text{K}_2\text{SO}_4$  with  $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ,

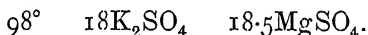
whose boiling points are respectively  $103^\circ$  and  $102^\circ$ .

What now is the composition of the solutions corresponding? Two measurements of solubility must be added to determine the course, on the one hand of the curve KJ, on the other of LH, to the right of the boundary HJ between schönite and potassium-astrakanite. These curves relate to saturation with potassium-astrakanite and respectively magnesium and potassium sulphate.

Saturation with potassium-astrakanite and magnesium sulphate in 100 parts of solution :



Saturation with potassium-astrakanite and potassium sulphate in 100 parts of solution :



By this means the lines JP and HQ can be introduced and prolonged to  $103^\circ$  (P) and  $102^\circ$  (Q) respectively.

The chief points and positions on the steam area are therefore given :

E, boiling point of water ( $100^\circ$ ).

ED, boiling point of magnesium sulphate solutions.

D, boiling point of saturated magnesium sulphate ( $108^\circ$ ).

DP, boiling point of solutions saturated with magnesium sulphate on increasing content of potassium sulphate.

P, boiling point of a solution saturated with magnesium sulphate and potassium-astrakanite ( $103^\circ$ ).

PQ, boiling point of solutions saturated with potassium-astrakanite.

Q, boiling point of a solution saturated with potassium-astrakanite and potassium sulphate ( $102^\circ$ ).

QF, boiling point of solutions saturated with potassium sulphate, on decreasing content of magnesium sulphate.

F, boiling point of a solution saturated with potassium sulphate ( $102^{\circ}$ ).

FE, boiling point of potassium sulphate solutions.

The plane passing through these points and lines is the boiling-limit of all the unsaturated solutions, and completes the figure on the right.

Two very good illustrations of Meyerhoffer's law, according to which, at a transition point, a sharp bend occurs in the solubility curve for the salt suffering transformation, but not for that which remains unchanged:

At K the magnesium sulphate is converted from hepta- to hexa-hydrate, while the potassium sulphate remains unchanged as schönite. Accordingly the magnesium sulphate line,  $L_1K_1J_1$ , shows a sharp bend; that of potassium sulphate,  $L_2K_2J_2$ , hardly any.

Similarly, at H the potassium sulphate remains as such, while the magnesium sulphate changes from schönite to astrakanite, and accordingly a bend occurs in  $L_1H_1Q_1$ , not in  $L_2H_2Q_2$ .

The relations are less conspicuous at J, where the potassium sulphate passes from schönite to astrakanite: the larger bend occurs in the diagram for potassium sulphate, it is true, but it is so small that it only becomes obvious on comparing the numbers:

Temp.	$K_2SO_4$	Increase per $1^{\circ}$	$MgSO_4$	Increase per $1^{\circ}$
$47.2^{\circ}$	9.9		27.9	
$72^{\circ}$	10.7	0.03	29	0.04
$85^{\circ}$	10.8	0.007	29.4	0.03

## 2. *Equilibrium between Ferric Chloride, Hydrochloric Acid, and Water.*

The distinction between the relations for equilibrium in this case and that previously described, and consequently also the special interest of the phenomena, lies in the noteworthy possibilities attending complete fusion. This has already been pointed out in the case of calcium chloride.



Here we have to study the same thing in the more complicated instance of a triple system. It is convenient to start in such a case with combinations of two at a time. Previously these were combinations of water and potassium sulphate on the one side, and water and magnesium sulphate on the other; here they are water and ferric chloride on one side, and water and hydrochloric acid on the other.

Let us represent the equilibrium between water and ferric chloride in Fig. 38, in the upper half, as the solubility curve for ferric chloride. It consists of five parts, relating to  $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ ,  $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$ ,  $\text{Fe}_2\text{Cl}_6 \cdot 5\text{H}_2\text{O}$ ,  $\text{Fe}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$ , and anhydrous  $\text{Fe}_2\text{Cl}_6$  respectively. Each part consists of two branches leading backwards, whose common point has a vertical tangent, and corresponds to a composition of the solution which is identical with that of the hydrate<sup>1</sup>.

The solubility of the hydrates of hydrochloric acid existing at low temperatures may be drawn in the under part of Fig. 38. We may here also start from the point  $o^\circ$  for pure water, and going along the curve of freezing points of solutions of hydrochloric acid reach the cryohydric point<sup>2</sup> for  $\text{HCl} \cdot 3\text{H}_2\text{O}$  at  $B'$ ; then follow the solution of that hydrate,  $B'C'D'$ , which at  $C'$  has the same composition as the solid hydrate<sup>3</sup>, and ends at  $D'$  with separation of the hydrate  $\text{HCl} \cdot 2\text{H}_2\text{O}$ ; then the curve  $D'E'F'$  for saturation with that hydrate, to its melting point at  $E'$  ( $-17.7^\circ$ ), and to separation of  $\text{HCl} \cdot \text{H}_2\text{O}$  at  $F'$ .

Let us now consider the possibilities when ferric chloride, hydrochloric acid, and water are all present. Their graphical representation is obtained by taking the planes of the above diagrams as projection planes: that on which ferric chloride was shown as vertical, that on which the behaviour of hydrochloric acid was expressed as horizontal plane of projection; the space between will then correspond to what occurs when  $\text{Fe}_2\text{Cl}_6$ ,  $\text{HCl}$ , and  $\text{H}_2\text{O}$  are all present.

<sup>1</sup> Roozeboom and Schreinemakers, *Zeitschr. f. Phys. Chem.* 15. 588.

<sup>2</sup> According to Pickering (*Berl. Ber.* 26. 28) at  $-85^\circ$ .

<sup>3</sup> The same at  $-25^\circ$ .

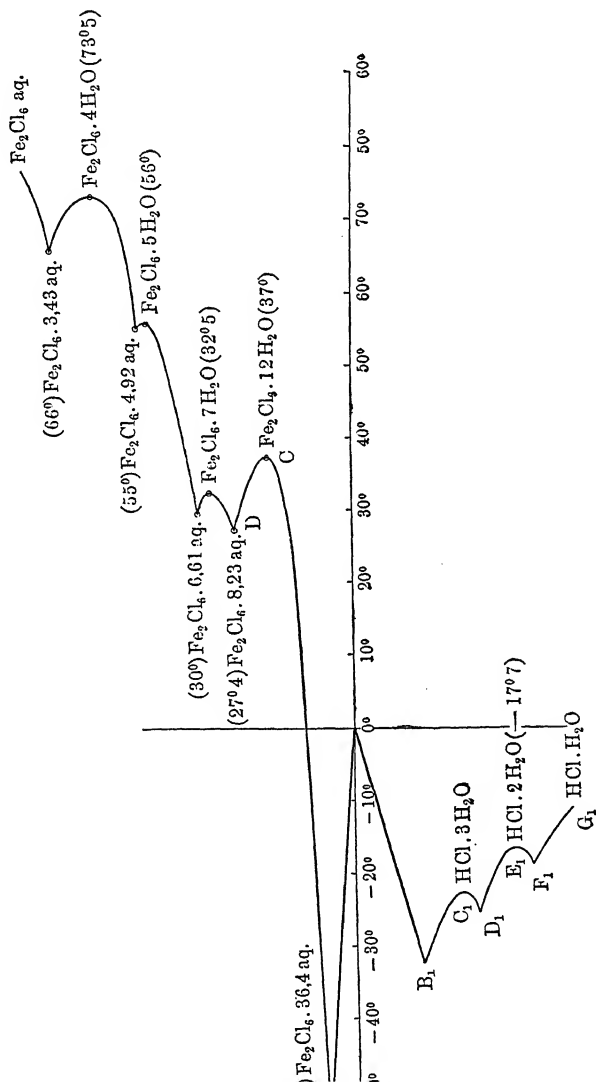


Fig. 38.

Let us develop the figure step by step, with the aid of Fig. 39, starting, say, from the curve BCD for saturated solutions of  $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$  at the point c, where the solution has the same composition, and which may, therefore, be called the melting point of that hydrate. If hydrochloric acid be added the melting point is lowered, as shown by the horizontal line CP, which, representing fall of temperature, runs from c towards the left. From each point

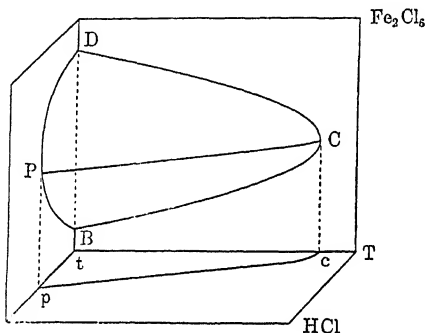


FIG. 39.

of the curve DCB a similar line may be drawn, and so we get a vaulted, somewhat shoe-like surface resting at BCD on the vertical plane, and swelling outwards from it towards the left. The form in question may be made more apparent by drawing a vertical plane at right angles to the axis of temperature, to represent a definite temperature  $t$ , and marking on it the curve DPB made by intersection with the curved surface.

Each hydrate curve has a similar surface, and where two of them meet, as in a line, e.g., starting from D (Fig. 38), the simultaneous existence is expressed of the two hydrates  $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$  and  $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$  with gradually increasing quantities of hydrochloric acid.

Corresponding surfaces starting from the horizontal plane are the expression of the freezing points of hydrates of hydrochloric acid, lowered by addition of ferric chloride,

and there remain to discuss only the points in which the lines of intersection of two surfaces before-mentioned may cut one another.

Take, e.g., surfaces touching  $OB$  (Fig. 38) on the one hand, and  $OB_1$  on the other, representing formation of ice: at  $o$  pure water,  $OB$  solutions of ferric chloride up to saturation with  $Fe_2Cl_6 \cdot 12H_2O$  at  $B$ ,  $OB_1$  solutions of hydrochloric acid up to saturation with  $HCl \cdot 3H_2O$ . Curves start from  $B$  and  $B_1$  which arise by intersection with the figures resting on  $BCD$  and  $B_1C_1D_1$  respectively. The first curve relates to lowering of the cryohydric temperature of  $Fe_2Cl_6 \cdot 12H_2O$  by  $HCl$ ; the second to lowering of the cryohydric temperature of  $HCl \cdot 3H_2O$  by  $Fe_2Cl_6$ . If the curves meet, we get a point representing simultaneous presence of ice,  $Fe_2Cl_6 \cdot 12H_2O$  and  $HCl \cdot 3H_2O$  in contact with a solution which, on withdrawal of heat, freezes to the same substances; in other words, the cryohydric point for a mixture of  $Fe_2Cl_6 \cdot 12H_2O$  and  $HCl \cdot 3H_2O$ .

The same may be said as to the existence of any other point of intersection.

Those compounds deserve special treatment which contain  $Fe_2Cl_6$ ,  $HCl$ , and  $H_2O$  and, like certain hydrates, show a melting point, i. e. change at definite temperature from completely solid to a clear melt. They are the compounds  $Fe_2Cl_6 \cdot 2HCl \cdot 4H_2O$ ,  $Fe_2Cl_6 \cdot 2HCl \cdot 8H_2O$ , and  $Fe_2Cl_6 \cdot 2HCl \cdot 12H_2O$ , which melt at  $45.7^\circ$ , at  $-3^\circ$ , and at  $-6^\circ$  respectively. Let us consider specially the behaviour of the first compound, and represent its melting point by projection at  $P$  (Fig. 40). The surfaces expressing the complete relations may be obtained most easily from two planes running vertically and horizontally parallel to the axis of temperature. The first expresses the lowering of melting point produced by addition or withdrawal of  $Fe_2Cl_6$ ; the latter that produced by addition or withdrawal of  $2HCl$ . The two sections  $pPr$  and  $spq$  meet at  $P$  in a sharp angle if the melting takes place without decomposition, so that the liquid produced may be regarded as consisting of molecules of

$\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 4\text{H}_2\text{O}$ .  $P$  is then the apex of a cone of which  $pPr$  and  $sPq$  are a pair of rectangular sections. If, on the contrary, the fusion is accompanied by partial decomposition, as is the case here, the lines  $sp$  and  $pq$  are parts of a curve which has a vertical tangent at  $P$ , and the whole forms a figure like part of an ellipsoid of rotation or a sphere. In both cases the behaviour at constant tem-

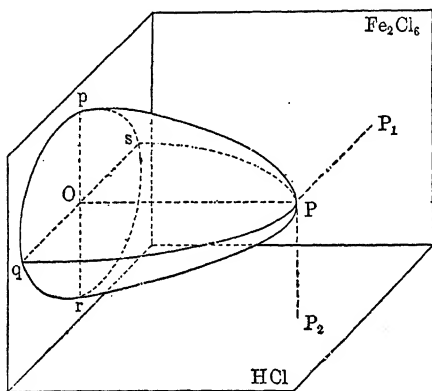


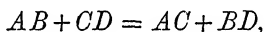
FIG. 40.

perature is expressed by the line arising by intersection with any vertical plane at right angles to the axis of temperature. It is a closed curve, and shows the solubility at constant temperature of the compound  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 4\text{H}_2\text{O}$ ; the solutions in question have a composition differing from  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 4\text{H}_2\text{O}$  (given by  $o$ ) at  $p$  by addition of  $\text{Fe}_2\text{Cl}_6$ , in  $pq$  by addition of both  $\text{Fe}_2\text{Cl}_6$  and  $\text{HCl}$ , at  $q$  by addition of  $\text{HCl}$  alone, in  $qr$  by addition of  $\text{HCl}$  but withdrawal of  $\text{Fe}_2\text{Cl}_6$ , in  $r$  by the latter alone, and so on.

The meeting of this surface with those relating to the hydrates already discussed, corresponds to the appearance of the latter alongside of the compound  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 4\text{H}_2\text{O}$ .

## G. Equilibrium between Four Substances.

This last category of the phenomena of equilibrium, which we have now to consider, has hitherto only been studied systematically in isolated cases. It possesses, however, a special interest, since it opens the possibility of including more complex chemical processes within the scope of similar more complete investigation. Since in presence of a single body only transformation is possible, of two bodies, dissociation and recombination, of three bodies, substitution; now that we assume the presence of four, we may deal with double decompositions according to the formula

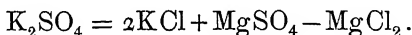


which is the most complicated of the reactions at present known.

The investigations in this direction are only in their first stages, and we can only describe the relations at constant temperature.

We shall be concerned with the work of Löwenherz<sup>1</sup> aiming at a knowledge of the mutual behaviour of four salts, KCl, MgCl<sub>2</sub>, MgSO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, and water.

The four bodies which are involved may be treated as a whole composed of four parts, as e.g. K<sub>2</sub>SO<sub>4</sub> may be thought of as arising from potassium chloride and magnesium sulphate by withdrawal of magnesium chloride, according to the formula



At 25° the relations are as follows:—

## 1. Solubility of the single salts.

A. KCl	1,000 molecules H <sub>2</sub> O,	44 molecules K <sub>2</sub> Cl <sub>2</sub> .
B. MgCl <sub>2</sub>	„ „	108 „ MgCl <sub>2</sub> .
C. MgSO <sub>4</sub>	„ „	58 „ MgSO <sub>4</sub> .
D. K <sub>2</sub> SO <sub>4</sub>	„ „	12 „ K <sub>2</sub> SO <sub>4</sub> .

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 13. 459.

2. Combinations of the salts in pairs with a common ion.

KCl and  $K_2SO_4$ . Two lines represent the relations of solubility, for saturation with KCl and increasing content of  $K_2SO_4$  on the one hand, and for saturation with  $K_2SO_4$  and increasing content of KCl on the other: they meet on simultaneous saturation with the two salts, when the solution has the composition:

E. KCl,  $K_2SO_4$ : 1000 molecules  $H_2O$ , 42 molecules  $K_2Cl_2$ , 1.5 molecules  $K_2SO_4$ .

$K_2SO_4$  and  $MgSO_4$ . In consequence of the existence of the double sulphate  $MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$  (schönite) we have the following stages:—

Saturation with  $K_2SO_4$  with increasing  $MgSO_4$ -content to saturation with schönite at the composition:

F.  $K_2SO_4$ ,  $K_2Mg(SO_4)_2 \cdot 6H_2O$ .

1,000 molecules  $H_2O$ , 16 molecules  $K_2SO_4$ , 22 molecules  $MgSO_4$ .

Saturation with schönite with increasing  $MgSO_4$ -content to saturation with  $MgSO_4 \cdot 7H_2O$  at the composition:

G.  $K_2Mg(SO_4)_2 \cdot 6H_2O$ ,  $MgSO_4 \cdot 7H_2O$ .

1,000 molecules  $H_2O$ , 14 molecules  $K_2SO_4$ , 38 molecules  $MgSO_4$ .

Saturation with  $MgSO_4 \cdot 7H_2O$  with decreasing  $K_2SO_4$ -content, ending in the solution saturated with  $MgSO_4$  alone:

$MgSO_4$  and  $MgCl_2$ . On account of the existence of magnesium sulphate hexahydrate, we get in the same way:

H.  $MgSO_4 \cdot 7H_2O$ ,  $MgSO_4 \cdot 6H_2O$ .

1,000 molecules  $H_2O$ , 15 molecules  $MgSO_4$ , 73 molecules  $MgCl_2$ .

I.  $MgSO_4 \cdot 6H_2O$ ,  $MgCl_2 \cdot 6H_2O$ .

1,000 molecules  $H_2O$ , 14 molecules  $MgSO_4$ , 104 molecules  $MgCl_2$ .

$\text{MgCl}_2$  and  $\text{KCl}$ . On account of the existence of carnallite we have:

J.  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ .

1,000 molecules  $\text{H}_2\text{O}$ , 105 molecules  $\text{MgCl}_2$ , 1 molecule  $\text{K}_2\text{Cl}_2$ .

K.  $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ ,  $\text{KCl}$ .

1,000 molecules  $\text{H}_2\text{O}$ , 99 molecules  $\text{MgCl}_2$ , 1 molecule  $\text{K}_2\text{Cl}_2$ .

### 3. Triple combinations.

While the preceding is connected with what has been considered previously, and forms indeed only an application of it to special cases, the problem now before us is the essentially new part of the present section. Both the fundamental mode of treatment, and the graphical representation of it, deserve on that account a thorough discussion.

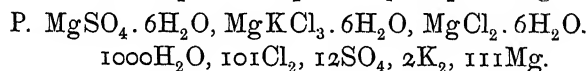
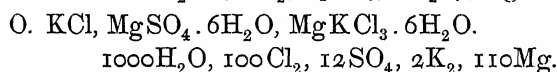
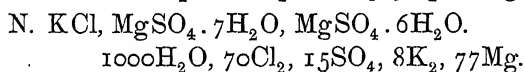
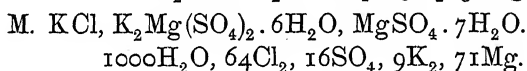
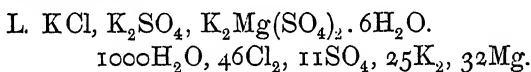
The most important point to note in the theory is the number of substances that must be in contact with the solution in order that it may have a given concentration at a given temperature. Note that the solutions in question may all be derived from any three of the salts,  $\text{KCl}$ ,  $\text{MgCl}_2$ ,  $\text{MgSO}_4$ , and  $\text{K}_2\text{SO}_4$ . Beginning, e.g., with  $\text{KCl}$ , the solution, at a given temperature, has a definite composition when one solid,  $\text{KCl}$  itself, is present; introducing  $\text{K}_2\text{SO}_4$ , the composition again becomes definite on presence of a second solid,  $\text{K}_2\text{SO}_4$  in this case; if finally we introduce a third salt,  $\text{MgSO}_4$ , the concentration again changes till a new salt separates out,  $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  in this case, and it becomes definite with three solids in contact with the solution.

Gibbs' phase rule leads to the same conclusion, stating that the composition of the so-called phases, i.e. mechanically separable parts, and therefore of the solution, is definite, when the number of phases exceeds the number of substances by one. 'Substances' here means the components which are necessary and sufficient to construct the



system—here three salts and water, or four in all. When five phases are present, therefore, the solution has a completely defined composition; of these five phases, the vapour over the solution is one, the solution itself the second, so that three solids suffice to define the composition of the solution.

If we considered the possibilities of triple salt combinations in the present case, in which the solids are  $\text{KCl}$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , or else  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ , not less than thirty-five arrangements are possible. Since, however,  $\text{K}_2\text{SO}_4$  and  $\text{MgSO}_4$  cannot exist side by side, but form schönite,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{KCl}$  carnallite, the former with  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , the hexahydrate, and so on, the number of possible arrangements is reduced, and only the following five remain, the solution in contact with them having the composition stated:—



We have now to represent all these results of experiment graphically. It seems appropriate to use four axes that cut one another like the edges of a regular octahedron at one of the vertices. Fig. 41 shows this. The content in  $\text{K}_2\text{SO}_4$ ,  $\text{MgSO}_4$ ,  $\text{MgCl}_2$ , and  $\text{KCl}$  is to be measured along these axes in such a way that the unit refers to corresponding quantities, and therefore for potassium chloride to  $\text{K}_2\text{Cl}_2$ . Let us represent the above results on the composition of the solution without any assumptions, by the

amount of three salts contained, e.g. the solution M saturated with potassium chloride, schönite, and magnesium sulphate :  
 $1000\text{H}_2\text{O}, 64\text{Cl}_2, 16\text{SO}_4, 9\text{K}_2, 71\text{Mg} = 1000\text{H}_2\text{O}, 7\text{MgSO}_4, 9\text{K}_2\text{SO}_4, 64\text{MgCl}_2.$

The respective quantities of  $\text{MgSO}_4$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{MgCl}_2$  are then represented along  $oc$ ,  $ob$ ,  $od$ . The first two as  $oc$  and  $ob$  give the point  $a$ , and from there the quantity of

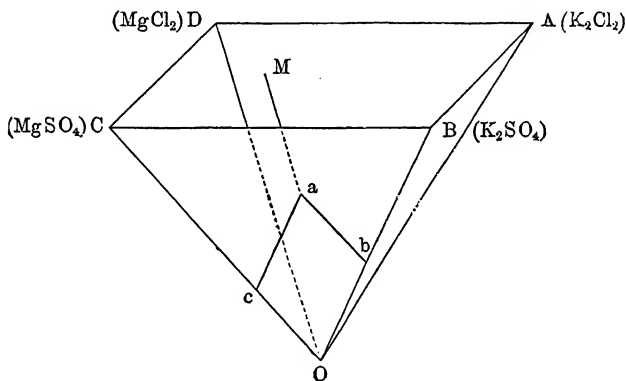


FIG. 41.

$\text{MgCl}_2$  is drawn by  $aM$  parallel to  $od$ , whence  $M$  is obtained, as representation of the required composition. This mode of representation clearly satisfies the condition that if the composition be expressed differently, e.g. instead of by  $1000\text{H}_2\text{O}, 7\text{MgSO}_4, 9\text{K}_2\text{SO}_4, 64\text{MgCl}_2$ , by the equivalent system  $1000\text{H}_2\text{O}, 9\text{K}_2\text{Cl}_2, 16\text{MgSO}_4, 55\text{MgCl}_2$ , the point  $M$  should lie in the same position as before.

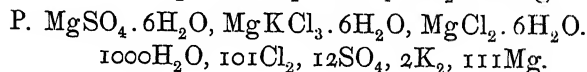
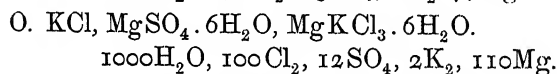
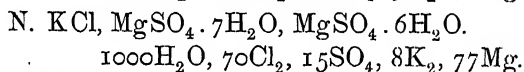
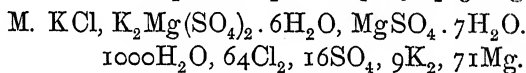
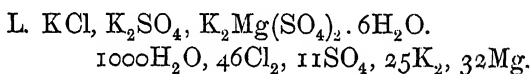
If we depict all the results of experiment thus, each result will correspond to one point. The entirety of these points is given in Figs. 42 and 43 by a horizontal and vertical projection, and the solubilities are expressed in the following manner:—

1. The simple salts on the four axes, i.e. the octahedral edges, A to D.

2. The data referring to pairs of salts with a common ion

system—here three salts and water, or four in all. When five phases are present, therefore, the solution has a completely defined composition; of these five phases, the vapour over the solution is one, the solution itself the second, so that three solids suffice to define the composition of the solution.

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amount of three salts contained, e.g. the solution *M* saturated with potassium chloride, schönite, and magnesium sulphate:  
 $1000\text{H}_2\text{O}, 64\text{Cl}_2, 16\text{SO}_4, 9\text{K}_2, 71\text{Mg} = 1000\text{H}_2\text{O}, 7\text{MgSO}_4, 9\text{K}_2\text{SO}_4, 64\text{MgCl}_2.$

The respective quantities of  $\text{MgSO}_4$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{MgCl}_2$  are then represented along *OC*, *OB*, *OD*. The first two as *oc* and *ob* give the point *a*, and from there the quantity of

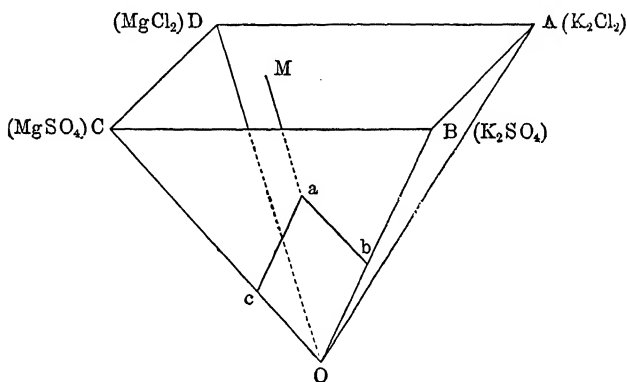


FIG. 41.

$\text{MgCl}_2$  is drawn by  $\alpha\text{M}$  parallel to *OD*, whence *M* is obtained, as representation of the required composition. This mode of representation clearly satisfies the condition that if the composition be expressed differently, e.g. instead of by  $1000\text{H}_2\text{O}, 7\text{MgSO}_4, 9\text{K}_2\text{SO}_4, 64\text{MgCl}_2$ , by the equivalent system  $1000\text{H}_2\text{O}, 9\text{K}_2\text{Cl}_2, 16\text{MgSO}_4, 55\text{MgCl}_2$ , the point *M* should lie in the same position as before.

If we depict all the results of experiment thus, each result will correspond to one point. The entirety of these points is given in Figs. 42 and 43 by a horizontal and vertical projection, and the solubilities are expressed in the following manner:—

1. The simple salts on the four axes, i.e. the octahedral edges, A to D.

2. The data referring to pairs of salts with a common ion

on the planes passing through the two axes in question, i.e. on the octahedral faces, E to K.

3. The solution saturated with three salts within the body of the octahedron at L to P.

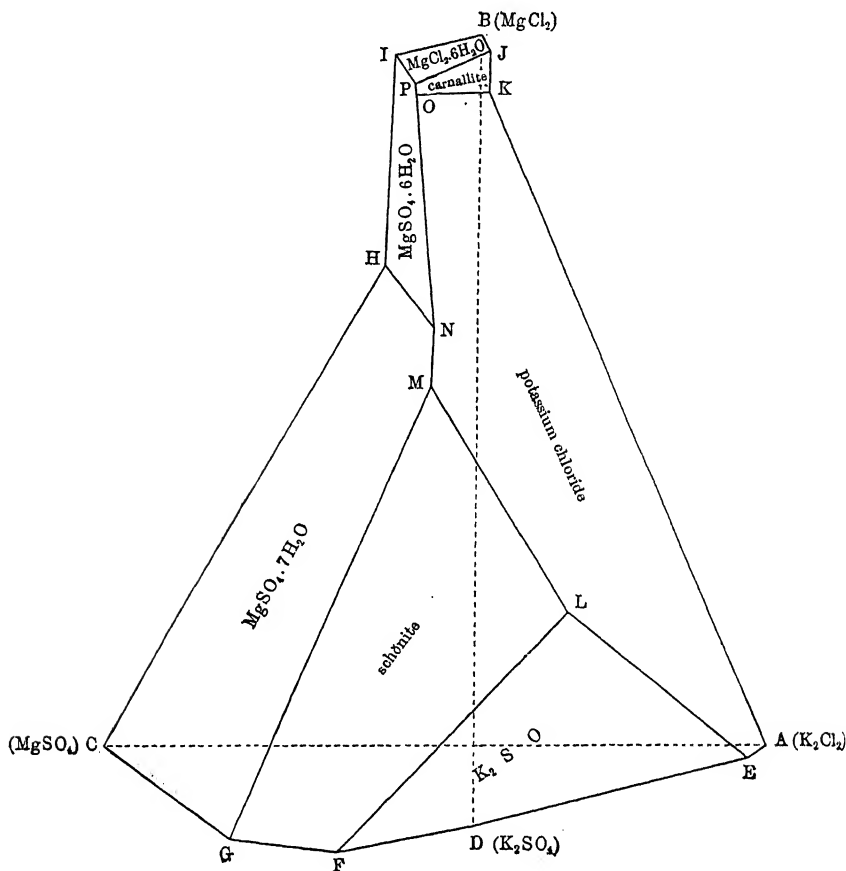


FIG. 42.

The graphical representation may now be completed by a set of lines which represent the solubility for two salts on increasing content of a third. Thus E represents saturation with KCl and  $K_2SO_4$ , whilst L stands for the same in

presence of solid schönite. E and L may, therefore, be joined by a line which represents saturation with  $\text{KCl}$  and  $\text{K}_2\text{SO}_4$

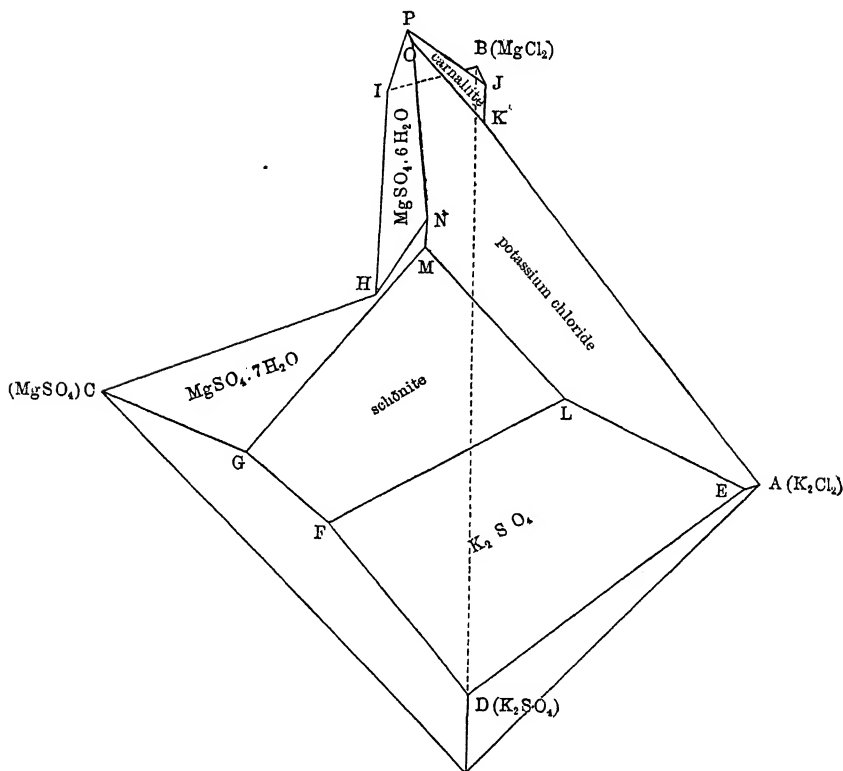


FIG. 43.

on gradually increasing content of magnesium, till it leads at L to separation of schönite.

The system of lines so produced divides the whole into areas representing each saturation with a definite salt :

Saturation with  $\text{K}_2\text{SO}_4$  : DELF.

„ „ schönite : GFLM.

„ „  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  : GCHNM.

„ „  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  : HNOPI.

Saturation with  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  : BIPJ.

„ „  $\text{MgKCl}_3 \cdot 6\text{H}_2\text{O}$  : JPOK.

„ „  $\text{KCl}$  : AELMNOK.

A line then represents saturation with the two salts whose areas are separated by it; a point, saturation with the three salts whose areas meet there.

The space between the octahedral faces and the figure just described represents unsaturated solutions; that outside the figure, supersaturated solutions.

## § 2. CHEMICAL EQUILIBRIUM FROM THE MOLECULAR-MECHANICAL POINT OF VIEW.

In the preceding section, which on p. 13 was headed 'Chemical Equilibrium viewed in its External Aspects,' we were concerned, on the chemical side with determinations of relative masses, and on the physical with determinations of temperature and pressure, and sometimes of volume.

We have now to go further, especially with regard to the chemical aspect, and the question arises whether by going further we may gain a deeper insight into the laws that regulate equilibrium.

As far as single substances are concerned, progress lies in determining molecular weight, constitution, configuration, and so belongs to the second part of 'Chemical Statics.' Here the chief interest is in a more complete knowledge of homogeneous mixtures, gases or solutions, which, amongst other things, play a part in the phenomena of equilibrium.

From the purely thermo-dynamic point of view one might be inclined to content oneself with the empirical composition of such a homogeneous mixture, since under given circumstances, e. g. of temperature and pressure, only one definite arrangement of matter is in equilibrium, and that is given by the quantitative composition. Still, as will be seen below, by working from molecular and atomistic conceptions, it is possible to develop laws, verified by experiment, which

it has not so far been possible to obtain in the purely thermo-dynamic method. On the other hand, one has often to deal with states of apparent equilibrium, which endure so long, that they are of the first consequence in considering the final state of equilibrium to be reached. In the same way, homogeneous mixtures of the same composition may have an apparently stable and yet different structure. Take, e. g., two equally concentrated solutions of laevo- and dextro-tartaric acid. They remain for a long time unchanged, as if they were in equilibrium; measurements of equilibrium even, such as a determination of the avidity, may be made, although eventually the true equilibrium is attained in the form of the inactive mixture, into which tartaric acid changes more rapidly when heated.

Since the chief interest is in the relations of equilibrium occurring through the action of homogeneous mixtures, the case of homogeneous equilibrium must be dealt with first. The results gained may then be applied to heterogeneous equilibrium; whilst, thirdly, we shall have the general conclusions, and connexion with the rules already discussed.

Hence the subject may be divided as follows:—

A. Homogeneous equilibrium.

B. Heterogeneous equilibrium.

C. General conclusions. Connexion with the rules already developed, and extension of them.

### A. Homogeneous Equilibrium.

#### 1. *Relations at Constant Temperature.*

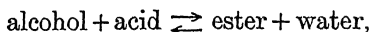
(a) *Equilibrium in gases, discussed theoretically.* The laws which may be expected to hold for equilibrium in mixtures of gases can only be deduced theoretically for the ideal case of extreme dilution.

The relation so obtained was, essentially, formulated by Guldberg and Waage<sup>1</sup>. In the exposition in question, the

<sup>1</sup> *Études sur les Affinités Chimiques.* Christiania, 1867.



so-called active mass, i.e. the mass of a body in unit volume, is taken as regulating the influences on the state of equilibrium ; thus, in dealing with the velocity of esterification,



the action of the first two bodies may be expressed by

$$k_1 M_a M_s,$$

where  $M_a$  and  $M_s$  are respectively the active masses of alcohol and acid, while  $k_1$  is a constant of affinity. The reverse action of the ester and water is similarly

$$k_2 M_e M_w,$$

and the condition of equilibrium

$$k_1 M_a M_s = k_2 M_e M_w.$$

In the more recent development of these laws the active mass occurs again, as the concentration ; but the deduction of the fundamental equation is different, and allows of its application only to the case of extreme dilution.

The deduction may be made in two different ways, the kinetic and the thermo-dynamic.

In the deduction from a kinetic basis<sup>1</sup>, equilibrium is regarded as the result of two opposite reactions proceeding with the same velocity. The velocity in question, or the amount of reaction in the unit of volume (cub. metre), is proportional to the mass of the substance present in that volume (expressed, say, in kilogram-molecules), i.e. to the concentration of the reacting substance if its molecules suffer conversion of themselves (unimolecular reaction). If, on the contrary, mutual action is necessary to bring about the reaction, the velocity of conversion, under given circumstances (of temperature, &c.), is proportional to the number of collisions between the molecules involved in the reaction. The number is with sufficient dilution propor-

<sup>1</sup> Van 't Hoff, *Berl. Ber.* 1877, p. 669.

tional to the concentration of each, and so, in the above case, the rate of esterification  $\frac{dC_e}{dt}$  is given by the equation

$$\frac{dC_e}{dt} = k_1 C_a C_s,$$

in which  $k_1$  is the velocity constant which expresses how much ester is formed in unit volume and in unit time, with concentrations unity. So also for the decomposition of the ester we have

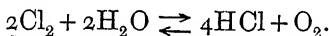
$$-\frac{dC_e}{dt} = k_2 C_e C_w,$$

and therefore the equilibrium condition

$$k_1 C_a C_s = k_2 C_e C_w.$$

A similar expression may be obtained on thermo-dynamic grounds, e. g. by the following cyclic process:—

We will consider the equilibrium obtaining at high temperatures between chlorine and steam on the one hand, and hydrochloric acid and oxygen on the other, obtained for instance by heating a mixture of the first two gases for a sufficient length of time in a closed space<sup>1</sup>. The equilibrium is symbolically



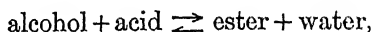
In two spaces A and B (Fig. 44) the above gaseous mixtures are present at the same temperature; equilibrium has been reached in both, but the ratios of masses or of volumes are different, and consequently also the concentrations. We will call these

$$\begin{array}{cccc} C_{\text{Cl}_2}, & C_{\text{H}_2\text{O}}, & C_{\text{HCl}}, & C_{\text{O}_2} \text{ in A,} \\ c_{\text{Cl}_2}, & c_{\text{H}_2\text{O}}, & c_{\text{HCl}}, & c_{\text{O}_2} \text{ in B.} \end{array}$$

The reversible cyclic process to be carried out consists in the conversion to and fro of the quantities occurring in the equation, i. e. of  $2\text{Cl}_2$  and  $2\text{H}_2\text{O}$ . That is to be accomplished by the cylinder c and piston d, which by means of a par-

<sup>1</sup> Hautefeuille, *Compt. Rend.* 109. 641; Le Chatelier, l. c. 664.

so-called active mass, i.e. the mass of a body in unit volume, is taken as regulating the influences on the state of equilibrium; thus, in dealing with the velocity of esterification,



the action of the first two bodies may be expressed by

$$k_1 M_a M_s,$$

where  $M_a$  and  $M_s$  are respectively the active masses of alcohol and acid, while  $k_1$  is a constant of affinity. The reverse action of the ester and water is similarly

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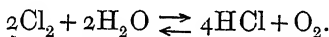
$$-\frac{dC_e}{dt} = k_2 C_e C_w,$$

and therefore the equilibrium condition

$$k_1 C_a C_s = k_2 C_e C_w.$$

A similar expression may be obtained on thermo-dynamic grounds, e. g. by the following cyclic process:—

We will consider the equilibrium obtaining at high temperatures between chlorine and steam on the one hand, and hydrochloric acid and oxygen on the other, obtained for instance by heating a mixture of the first two gases for a sufficient length of time in a closed space<sup>1</sup>. The equilibrium is symbolically



In two spaces A and B (Fig. 44) the above gaseous mixtures are present at the same temperature; equilibrium has been reached in both, but the ratios of masses or of volumes are different, and consequently also the concentrations. We will call these

$$\begin{array}{cccc} C_{\text{Cl}_2}, & C_{\text{H}_2\text{O}}, & C_{\text{HCl}}, & C_{\text{O}_2} \text{ in A,} \\ c_{\text{Cl}_2}, & c_{\text{H}_2\text{O}}, & c_{\text{HCl}}, & c_{\text{O}_2} \text{ in B.} \end{array}$$

The reversible cyclic process to be carried out consists in the conversion to and fro of the quantities occurring in the equation, i. e. of  $2\text{Cl}_2$  and  $2\text{H}_2\text{O}$ . That is to be accomplished by the cylinder c and piston d, which by means of a par-

<sup>1</sup> Hautefeuille, *Compt. Rend.* 109. 641; Le Chatelier, l. c. 664.

tition *ab*, allowing only chlorine to pass, introduces the gas into A; steam enters in the same way, whilst at the same time and in a similar manner oxygen and hydrochloric acid are removed by the cylinder and piston E and F. If the gases in question have the same concentrations as in A, no change in the condition of A occurs, whilst chlorine and water are converted into hydrochloric acid and oxygen. Afterwards the gases produced—oxygen and hydrochloric acid—may be expanded or compressed, reversibly and at constant temperature, till they have the concentrations

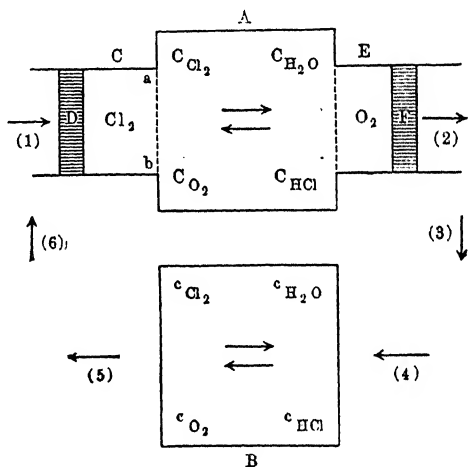


FIG. 44.

obtaining in B; the reconversion into chlorine and water may be carried out as above, and the products obtained reduced to the concentration obtaining in A.

Since in this reversible cyclic process the temperature remains constant, no heat is converted into work; the sum of the separate amounts of work done is therefore zero. We will express this as

$$(1) + (2) + (3) + (4) + (5) + (6) = 0,$$

in which (1) is the work spent in introducing the chlorine and steam; but that work is recovered on the reproduction

of the gases, on account of the constancy of  $PV$  for the same temperature and mass. Hence

$$(1) + (5) = 0.$$

Similarly  $(2) + (4) = 0,$

and there remains  $(3) + (6) = 0.$

That is, the net work spent in the change of concentration is zero. This work is, in calories, for any gas

$$A \int_v^v P dV,$$

in which, for a kilogram-molecule,

$$APV = 2T.$$

Hence it is  $2T \int_v^v \frac{dV}{V} = 2T \log \frac{v}{V},$

and, since the volume is inversely as the concentration,

$$2T \log \left( \frac{v}{V} \right) = 2T \log \left( \frac{C}{c} \right).$$

Therefore  $(6) = 2T \log \frac{C_{O_2}}{c_{O_2}} + 4 \times 2T \log \frac{C_{HCl}}{c_{HCl}},$

and  $(3) = 2 \times 2T \log \frac{c_{Cl_2}}{C_{Cl_2}} + 2 \times 2T \log \frac{c_{H_2O}}{C_{H_2O}},$

whence after division by  $2T$

$$\log \frac{C_{O_2}}{c_{O_2}} + 4 \log \frac{C_{HCl}}{c_{HCl}} = 2 \log \frac{c_{Cl_2}}{C_{Cl_2}} + 2 \log \frac{c_{H_2O}}{C_{H_2O}},$$

and putting the concentrations belonging to each space together,  $C$  on one side,  $c$  on the other :

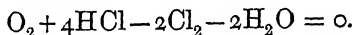
$$\begin{aligned} \log C_{O_2} + 4 \log C_{HCl} - 2 \log C_{Cl_2} - 2 \log C_{H_2O} &= \log c_{O_2} \\ &+ 4 \log c_{HCl} - 2 \log c_{Cl_2} - 2 \log c_{H_2O}, \end{aligned}$$

from which it appears that that function of the concentrations is constant which is obtained by summing the logarithms of each concentration multiplied by the number of times the molecule referred to occurs in the equation to

the reaction, those on the left-hand side ( $\text{Cl}_2$  and  $\text{H}_2\text{O}$ ) being counted negative. Quite generally we may say

$$\sum n \log C = \text{const.},$$

in which  $n$  is the number of molecules,  $C$  the concentration in question, remembering that the terms on the left-hand side appear as negative, as in the equation of the form :



For the above example on esterification-equilibrium, since the number of each molecule is unity,

$$\log C_e + \log C_w - \log C_a - \log C_s = \text{const.},$$

or

$$\frac{C_e C_w}{C_a C_s} = \text{const.},$$

in agreement with the condition previously worked out.

(b) *Equilibrium in gases. Applications.* In dealing with applications, we come now to the methods by which we may determine the quantity of each substance present in a gaseous mixture in the state of chemical equilibrium, or more generally in any homogeneous mixture. Two ways are open.

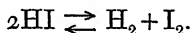
On the one hand, adopting the direct method, we may determine quantitatively one or more components by means of any chemical or physical process of separation. This method is at first sight preferable, as being direct; only there is the danger that the separation itself may upset the state of equilibrium to be studied, and so lead to an incorrect result. If that possibility cannot be excluded, the second method is to be adopted, in which the material is brought untouched under investigation, but then only indicates its composition in an indirect manner.

(a) *Direct analysis. Equilibrium in gaseous hydriodic acid.* Direct analysis is applicable when we are concerned with an equilibrium which closes a very slow reaction. The displacement of equilibrium taking place during the analysis is then only very slight. We may

here with advantage make use of the well-known property of reactions, that their velocity is very greatly reduced by fall of temperature, becoming only one-half to one-third as great for each  $10^{\circ}$ . Hence by rapid cooling of the mixture in equilibrium, we get a condition in which analysis gives reliable results, and it is only necessary to bear in mind the possibility of a change in the equilibrium due to change of temperature.

The investigation has been carried out for hydriodic acid<sup>1</sup> by heating similarly, on the one hand bulbs filled with the gas, and on the other bulbs containing a weighed amount of iodine and a measured volume of hydrogen. The final state proved to be the same for the same proportions of the elements.

To carry out the quantitative test of the equilibrium condition, we have to work out the consequences of the equation



The fundamental equation

$$\Sigma n \log C = \text{const.},$$

in which terms relating to the first system are to be considered negative, gives for the case in question

$$\log C_{\text{I}_2} + \log C_{\text{H}_2} - 2 \log C_{\text{HI}} = \text{const.},$$

or

$$\frac{C_{\text{I}_2} C_{\text{H}_2}}{C_{\text{HI}}^2} = K,$$

in which  $K$  is what is termed the reaction-constant.

A simple deduction may be first discussed: the condition of equilibrium is independent of the volume, and so also of the pressure. If  $p$ ,  $q$ , and  $s$  are the total masses of iodine, hydrogen, and their compound in equilibrium, and  $V$  the volume, we have

$$C_{\text{I}_2} = \frac{p}{V}, \quad C_{\text{H}_2} = \frac{q}{V}, \quad C_{\text{HI}} = \frac{s}{V}.$$

<sup>1</sup> Lemoine, *Ann. d. Chim. et d. Phys.* [5] 12. 145; Bodenstein, *Zeitschr. f. Phys. Chem.* 22. 1.



therefore

$$\frac{pq}{s^2} = K,$$

so that the relation is determined independently of the volume.

Hence, instead of calculating by means of the concentrations, we may do so with the masses, best expressed in molecular units, and the magnitude of the molecular unit chosen has no influence on the value of  $K$ .

Thus if the quantity of hydrogen present originally be = 1 in molecular units, the iodine =  $a$ . Let  $2\gamma$  molecules of hydriodic acid be formed from those, so that  $1-\gamma$  and  $a-\gamma$  hydrogen and iodine remain. The equilibrium condition is therefore

$$\frac{(1-\gamma)(a-\gamma)}{4\gamma^2} = K,$$

whence

$$2\gamma = \frac{1+a - \sqrt{(1+a)^2 - 4as}}{s} \quad (\text{where } s = 1-4K).$$

In the following table the values of  $2\gamma$  calculated from this equation are compared with the amounts of hydriodic acid found: the numbers refer to  $440^\circ$ . The quantity of hydrogen is expressed as the volume of gas in cub. centimetres at  $0^\circ$  and 760 mm., and the iodine similarly, so that all may be reduced to molecular units. The hydriodic acid then also appears as cub. centimetres at  $0^\circ$  and 760 mm.

$H_2$	$I_2$	$\frac{I_2}{H_2} = a$	HI (obs.)	$2\gamma$
20.57	5.22	0.254	10.22	10.19
20.6	14.45	0.702	25.72	25.54
20.53	25.42	1.238	34.72	34.96
20.55	31.89	1.552	36.98	37.13
20.41	52.8	2.538	38.68	39.01
20.28	67.24	3.316	39.52	39.25
19.99	100.98	5.048	39.62	39.28

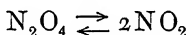
The value of  $K$  is estimated at 0.02 from the mean of the observations, so that  $s = 1-4K = 0.92$  and

$$2\gamma = \frac{1+a - \sqrt{a^2 - 3.68a + 1}}{0.92}.$$

( $\beta$ ) *Indirect analysis.* *Investigation by means of molecular weight.* *Nitric peroxide.* In dealing with indirect modes of determination, here and later, we will choose cases so far as possible that make use of the leading methods. In the first place, both physical and chemical indirect methods are employed. Amongst the latter figure especially those that may be called catalytic processes of determination: the quantity of a substance in equilibrium is measured by the catalytic action it effects, i. e. an action in which the quantity of the acting substance remains unchanged; no displacement of equilibrium seems to occur in such cases<sup>1</sup>. The physical methods are very various; a first group is based on molecular weight determinations, in their various forms, and will be discussed in the case of nitric peroxide.

The density<sup>2</sup> of gaseous nitric peroxide shows that the gas consists of  $N_2O_4$  and  $NO_2$  mixed in varying proportions, and colorimetric researches<sup>3</sup> have verified that qualitatively and quantitatively.

The equation of equilibrium



leads, by application of the fundamental equation

$$\sum n \log C = \text{const.},$$

to

$$\frac{C_{NO_2}^2}{C_{N_2O_4}} = K.$$

If  $1-x$  kilogram-molecules  $N_2O_4$  are present with  $2x$  kilogram-molecules  $NO_2$  in  $V$  cub. metres, the above equation may be written

$$\frac{x^2}{(1-x)V} = \frac{K}{4} = \text{const.} \quad (1)$$

Here, therefore, the volume is of influence on the equili-

<sup>1</sup> Shields, *Zeitschr. f. Phys. Chem.* 12. 185.

<sup>2</sup> Natanson, *Wied. Ann.* 24. 465, 27. 613.

<sup>3</sup> Salet, *Comptes Rend.* 67. 488.

brium condition. If now, as in Natanson's research, the density  $D$  referred to air, the pressure and the temperature are known, since 3.179 is the density of  $N_2O_4$  referred to air:

$$\frac{3.179}{1+x} = D.$$

Thus, starting say with the molecular quantity  $N_2O_4$ , by conversion of  $xN_2O_4$  into  $2xNO_2$ , the molecular quantity, and so the volume is increased from 1 to  $1+x$ , and the density accordingly reduced to the  $\frac{1}{(1+x)}$  part.

The volume  $V$ , on the one hand, in which a kilogram-molecule is present, may be calculated from  $x$ , for

$$APV = 2T$$

for the molecular quantity, so that for  $1+x$  molecule

$$APV = 2(1+x)T.$$

Introducing this in the above equation (1) we have

$$\frac{AP \left( \frac{3.179}{D} - 1 \right)^2}{2T \frac{3.179}{D} \left( 2 - \frac{3.179}{D} \right)} = \text{const.};$$

so that if the temperature remains the same

$$\frac{P(3.179-D)^2}{2D-3.179} = \text{const.}$$

For verification, the logarithm of the constant, as derived from  $P$  and  $D$ , is shown in the following table:—

Temp.	$D$	$P$	log. constant.
21.7°	2.144	59.7	1.76
21.3°	2.318	117.6	1.78
21.7°	2.486	230.6	1.79
21.3°	2.589	327.1	1.76
21.3°	2.599	367.1	1.79
21.6°	2.674	492.1	1.75
21.8°	2.709	617.6	1.76

(c) *Equilibrium in solutions of non-electrolytes, discussed theoretically.* The regularities observed as to the chemical equilibrium of non-electrolytes in dilute solution are of precisely the same form as in gases:

$$\Sigma n \log C = \text{const.},$$

and may be deduced in the same manner by the aid of the conception of a membrane permeable for the solvent only.

Another course may be followed, remembering that any substance is capable of evaporation at the customary temperature, and so also shows a certain pressure when in solution. Imagine then, above the solution in which the equilibrium in question occurs, a closed space in which the partially vaporized substances from the solution are again in equilibrium; then for the concentration of the vapours we have the relation

$$\Sigma n \log C = \text{const.}$$

But for a dilute solution of a non-electrolyte the concentration  $c$  is connected with that,  $C$ , of the vapour above it by Henry's law:

$$C = ac,$$

in which  $a$  is a number calculated from the ratio by absorption. Hence

$$\Sigma n \log ac = \text{const.}$$

Therefore

$$\Sigma n \log c = \text{const.} - \Sigma n \log a,$$

that is

$$\Sigma n \log c = \text{const.}$$

Just the same relation therefore holds as in gases, and the reaction constant in any solvent may be calculated from that for the gaseous mixture by means of the absorption coefficients.

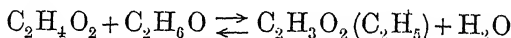
(d) *Equilibrium in solutions of non-electrolytes. Applications.* (a) *Direct analysis.* *Equilibrium in esterification.* Here<sup>1</sup> the conditions for the expected rule were

<sup>1</sup> Berthelot and Péan de St. Gilles, *Ann. de Chim. et de Phys.* 65, 66, 68.

not entirely fulfilled, since the dilution of the system was insufficient; still, working with very concentrated mixtures of alcohol and acid, the agreement with the theoretical conclusions is satisfactory enough, and offers extensive data for a suitable application of the theory. It takes the following form<sup>1</sup>:—From the fundamental equation

$$\Sigma n \log C = \text{const.}$$

and the equation of reaction



it follows that for equilibrium

$$\frac{C_e C_w}{C_s C_a} = K,$$

where  $C_e$ ,  $C_w$ ,  $C_s$ , and  $C_a$  are the concentrations of ester, water, acid, and alcohol.

Starting with the molecular quantity of acid in a volume  $V$ , if in that volume there be originally  $k$  molecules of alcohol and also  $q$  molecules of water, then if finally  $u$  molecules of ester have been formed:

$$C_e = \frac{u}{V} \quad C_w = \frac{q+u}{V} \quad C_s = \frac{1-u}{V} \quad C_a = \frac{k-u}{V},$$

whence

$$\frac{u(q+u)}{(1-u)(k-u)} = K,$$

where, as with hydriodic acid, the volume does not enter into the final condition.

To determine  $K$  we have that at the temperature of the determinations, when equivalent quantities of alcohol and acid are mixed, just  $\frac{2}{3}$  are converted into ester, so that for

$$q = 0 \text{ and } k = 1, \quad u = \frac{2}{3} \text{ and } K = 4,$$

and the equation becomes

$$u(q+u) = 4(1-u)(k-u),$$

whence in general

$$u = \frac{1}{8} \{ 4(k+1) + q - \sqrt{16(k^2 - k + 1) + 8q(k+1) + q^2} \}.$$

<sup>1</sup> Van 't Hoff, *Berl. Ber.* 1877, p. 669.

We will choose that one of the experiments in which a gradually increasing amount of alcohol was added to a fixed amount of acid without water. Then

$$q = 0 \text{ and } u = \frac{2}{3} (k + 1 - \sqrt{k^2 - k + 1}).$$

The following observed values may be compared with the calculated:—

$k$	$u$ (obs.)	$u$ (cal.)	$k$	$u$ (obs.)	$u$ (cal.)
0.05	0.05	0.049	0.67	0.519	0.528
0.08	0.078	0.078	1	0.665	0.667
0.18	0.171	0.171	1.5	0.819	0.785
0.28	0.226	0.232	2	0.858	0.845
0.33	0.293	0.311	2.24	0.876	0.864
0.5	0.414	0.423	8	0.966	0.945

Secondly, a series in which water in gradually increasing quantity was added beforehand to a mixture of acid and alcohol in equivalent amounts. Then

$$k = 1 \text{ and } u = \frac{1}{8} \{8 + q - \sqrt{16(1 + q) + q^2}\}.$$

$q$	$u$ (obs.)	$u$ (cal.)	$q$	$u$ (obs.)	$u$ (cal.)
0	0.665	0.667	2	0.458	0.465
0.5	0.614	0.596	4	0.341	0.368
1	0.547	0.542	6.5	0.284	0.288
1.5	0.486	0.5	11.5	0.198	0.212

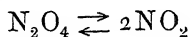
(β) *Indirect analysis.* *Colorimetric study of nitric peroxide dissolved in chloroform.* Salet's researches (p. 111) have shown that the fall of density of nitric peroxide produced by rise of temperature is accompanied by a darkening of the gas, and that the colorimetric results agree with the densimetric if we assume that  $N_2O_2$  is colourless and  $NO_2$  coloured. Cundall<sup>1</sup> carried out a similar colorimetric study of nitric peroxide dissolved in chloroform, and by its power of absorption calculated how much of the peroxide was in the dissociated form, i.e. as  $NO_2$ . Ostwald<sup>2</sup> showed that the results are in agreement with the relation

$$\Sigma n \log C = \text{const.},$$

<sup>1</sup> *Journ. Chem. Soc.* 1891, p. 1076.

<sup>2</sup> *l. c.* 1892, p. 242.

which for the reaction



takes the form (cf. p. 111)

$$\frac{x^2}{(1-x)V} = \text{const.},$$

in which  $x$  stands for the quantity present as  $\text{NO}_2$ ,  $1-x$  as  $\text{N}_2\text{O}_4$ , and  $V$  the volume in which both occur.

In the expression of the results, the total amount  $M$  in volume per cent. of the solution in chloroform is given. If the specific gravity of the liquid nitric peroxide at the temperature considered is  $S$ , there are  $10SM$  kilograms per cub. metre, i. e.  $\frac{10SM}{92}$  kilogram-molecules ( $\text{N}_2\text{O}_4=92$ ). The volume  $V$  occupied by a kilogram-molecule is accordingly

$$V = \frac{92}{10SM} = \frac{9.2}{SM}.$$

The  $\text{NO}_2$  present is expressed by  $r$ , the quantity of  $\text{NO}_2$  contained in the same quantity of liquid peroxide at  $0^\circ$ , a mode of expression arrived at by comparison with the gaseous compound in a known degree of dissociation ( $30^\circ$  and 755.8 mm.). It appeared from this that the liquid peroxide at  $0^\circ$  contains 0.0468 per cent. of  $\text{NO}_2$  by weight;  $r$  must accordingly be multiplied by 0.000468 to obtain  $x$ . We have then the relation

$$\frac{x^2}{(1-x)V} = \frac{(0.000468r)^2}{(1-0.000468r) \frac{9.2}{SM}} = \text{const.},$$

whence

$$\frac{r^2 M}{1-0.000468r} = \text{const.},$$

and for small values of  $r$  very approximately

$$r^2 M = \text{const.}$$

The following table shows how far the measurements satisfy the prediction:—

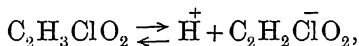
$M$	$r$	$r^2M$		$M$	$r$	$r^2M$
9.93	3.8	143		2	7	98
6	4.4	116		1.6	8.06	104
4.8	4.5	97		1.4	8.7	106
3.6	5.7	117		0.8	11.2	100
2.5	6.5	105				

(e) *Equilibrium in solutions of half-electrolytes, discussed theoretically.* When electrolytic dissociation occurs in solutions, so that, besides undissociated molecules, their products of dissociation as ions must be assumed to exist, a new factor enters into the phenomena of equilibrium, viz. the interaction between the undissociated molecules and the ions.

We have, therefore, next to take this process into account.

The question as to this is answered by Ostwald's law of dissociation<sup>1</sup> for the weak acids and bases, whose electrolytic dissociation is slight for ordinary concentrations, and which may therefore be spoken of as half-electrolytes. Assuming that the electrolytic conductivity is effected by the free ions present in the solution only, then the conductivity calculated for a fixed mass of dissolved substance is a measure of the fraction of it dissociated into ions, and that is the case too with the so-called molecular conductivity<sup>2</sup>, referred to the normal solution. The latter increases with the dilution, on account of increasing dissociation, and reaches the limiting value  $\mu_\infty$ , which corresponds to complete dissociation, so that the fraction  $\frac{\mu}{\mu_\infty}$  expresses directly the fraction dissociated.

Let us take here also the customary equation to the reaction, e. g. for solution of chloracetic acid:



i. e. on the one side the acid, on the other its two ions; then the fundamental equation

$$\sum n \log C = \text{const.}$$



leads immediately to

$$\frac{C_H C_{C_2H_2ClO_2}}{C_{C_2H_3ClO_2}} = K,$$

in which  $C_H$  and  $C_{C_2H_2ClO_2}$  express the (equal) concentrations of the ions, say  $C_j$ , while  $C_{C_2H_3ClO_2}$  is that of the unchanged acid  $C_s$ , or

$$\frac{C_j^2}{C_s} = K.$$

Now if there is a kilogram-molecule in  $V$  cub. metres, or a gram-molecule in  $V$  litres, then

$$C_j = \frac{\mu}{\mu_\infty V} \text{ and } C_s = \frac{1}{V} \left(1 - \frac{\mu}{\mu_\infty}\right),$$

and accordingly

$$\frac{\mu^2}{\mu_\infty (\mu_\infty - \mu) V} = K.$$

We give below a series of experiments, with the corresponding calculated and observed results<sup>1</sup>; they refer to monochloracetic acid at 14.1°.

$V$	$\mu$	$\frac{\mu}{\mu_\infty}$	$\frac{\mu}{\mu_\infty}$ calculated from $\log K = 3.2$
20	51.6	0.166	0.163
205	132	0.423	0.43
408	170	0.547	0.543
2060	251	0.806	0.801
4080	274	0.881	0.88
10100	295	0.948	0.944
20700	300	0.963	0.971
$\infty$	311	1	1

It should be noticed that hitherto no single case of ordinary non-electrolytic dissociation has been found to agree with the calculated results over so wide a range and so exactly.

Further, the degree of dissociation found in this way appears identical with that obtained by measurements of molecular weight or of freezing points. Electrolytic disso-

<sup>1</sup> Van 't Hoff and Reicher, *Zeitschr. f. Phys. Chem.* 2. 781.

ciation must cause the depression of the freezing point, and therefore also the molecular depression, which is calculated for the molecular weight in 100 parts of solution, to increase in the ratio

$$1 \text{ to } 1 - \frac{\mu}{\mu_{\infty}} + 2 \frac{\mu}{\mu_{\infty}} = 1 + \frac{\mu}{\mu_{\infty}}.$$

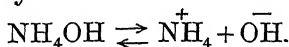
This quantity,  $\frac{1 + \mu}{\mu_{\infty}}$ , which is characteristic of the degree of dissociation, and which is often expressed by the letter  $i$ , may also be found by dividing the normal value of 18.7 of the molecular depression into that observed. Thus

$$1 + \frac{\mu}{\mu_{\infty}} = i = \frac{t_M}{18.7}.$$

In testing this relation Wildermann<sup>1</sup>, amongst others, found for dichloroacetic acid that the value of  $i$  derived from freezing-point measurements exceeds the quotient  $\frac{\mu}{\mu_{\infty}}$  (the fraction dissociated) by unity; as it should do.

Normality.	$i = \frac{t_M}{18.7}$	$\frac{\mu}{\mu_{\infty}}$	$i - \frac{\mu}{\mu_{\infty}} - 1$
0.002599	1.966	0.956	1.010
0.05177	1.911	0.913	0.998
0.1033	1.852	0.843	1.009
0.15447	1.763	0.806	0.957
0.2048	1.717	0.731	0.986
0.2778	1.69	0.703	0.987
		Mean	0.991

It may be added that, according to Bredig<sup>2</sup>, this law of dissociation holds for weak bases (ammonia and its derivatives) as well as for weak acids; hence in solutions of bases (e. g. ammonia) we may assume the state of equilibrium expressed by



(f) *Equilibrium in solutions of half-electrolytes. Appli-*

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 19. 242.

<sup>2</sup> *l. c.* 13. 289.

cations. *Indirect analysis by means of the conductivity.* Since in half electrolytes the relations of equilibrium are between the undissociated part and the ions simply, any equilibrium arrived at by the interaction of such half-electrolytes in solution may be calculated, provided only that no new bodies are produced which do not follow Ostwald's law of dissociation. Of the two possible cases—first, that half-electrolytes with a common ion, e.g. only weak acids with a common H-ion, and, second, that besides acids with the H-ion also bases with the OH-ion are present—the latter must be excluded at present, since in it salts are formed whose dissociation has not yet been studied.

First, then, let us turn to what takes place when two weak acids are brought together in dilute solution, say acetic and cyanacetic<sup>1</sup>.

Whilst for this case, without the aid of the dissociation theory, there is hardly anything to be said, that theory pictures a mutual action of the two acids which explains that the properties of the solutions—conductivity, rate of inversion of cane sugar, &c.—are not the mean between those of two solutions containing the acids separately. When one acid is mixed with another, the increased quantity of H-ions causes a displacement of equilibrium which can be followed out numerically.

The conditions of equilibrium in question may be simply expressed by means of the concentration of the various substances present in the solution:

*First acid.*

$C_{Z_1H}$

*Second acid.*

$C_{Z_2H}$

*Ions.*

$C_{Z_1} \quad C_{Z_2} \quad C_H$

that is, five unknowns, reduced to four by the necessary equality between the total positive and total negative ions,

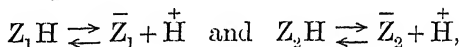
$$C_H = C_{Z_1} + C_{Z_2}.$$

<sup>1</sup> Wakemann, *Zeitschr. f. Phys. Chem.* 15. 159.

Two further equations are obtained by the known total mass of each acid present in unit volume,

$$C_{Z_1H} + C_{Z_1} = Z_1 \quad \text{and} \quad C_{Z_2H} + C_{Z_2} = Z_2,$$

and the remaining equations needed are supplied by considering the equilibria:



which lead to

$$\frac{C_{Z_1}C_H}{C_{Z_1H}} = K_1 \quad \text{and} \quad \frac{C_{Z_2}C_H}{C_{Z_2H}} = K_2.$$

The little Fig. 45 is perhaps suited to represent the conditions graphically; it expresses directly the concentrations involved, and the necessary equality between  $C_H$  and  $C_{Z_1} + C_{Z_2}$ , and shows that

the solution may be regarded as one containing the two acids in a partially

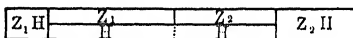


FIG. 45.

dissociated state, while the degree of dissociation, e.g. of the first acid, is expressed by the ratio  $C_{Z_1} : Z_1$ . This treatment allows also of calculating the molecular conductivity of the solution, and gives

$$\frac{\mu'_\infty C_{Z_1} + \mu''_\infty C_{Z_2}}{Z_1 + Z_2},$$

in which  $\mu'_\infty$  and  $\mu''_\infty$  are respectively the molecular conductivities of the acids  $Z_1H$  and  $Z_2H$  for infinite dilution.

To proceed now to a definite case, let us suppose solutions

$\frac{1}{3.208}$  normal of acetic acid and  $\frac{1}{240.6}$  normal of cyanacetic acid, and mix them together; then it follows from the above that in general there will be a displacement of equilibrium in each. Only in one case is that not so, and according to Arrhenius<sup>1</sup> when the concentration of hydrogen ions is the same in each solution before mixing: the solutions are then called isohydric. That is obvious from the conditions of equilibrium.

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 2. 284.

Before mixture we have:

1. Volume of the acetic acid solution  $V$  and concentrations  $C_{Z_1H}$  and  $C_H$  connected by the equation

$$\frac{C_H^2}{C_{Z_1H}} = K_1 = 0.000018 \quad (1)$$

2. Volume of the cyanacetic acid solution  $V_2$  and concentrations  $C_{Z_2H}$  and  $C_H$  connected by the equation

$$\frac{C_H^2}{C_{Z_2H}} = K_2 = 0.0037 \quad (2)$$

After mixing we have, without displacement of equilibrium:

Concentration of hydrogen ions  $C_H$

$$,, \quad ,, \quad \text{acid ions } Z_1 \quad C_H \frac{V_1}{V_1 + V_2}$$

$$,, \quad ,, \quad ,, \quad Z_2 \quad C_H \frac{V_2}{V_1 + V_2}$$

,, acids  $C_{Z_1H} \times \frac{V_1}{V_1 + V_2}$  and  $C_{Z_2H} \times \frac{V_2}{V_1 + V_2}$  respectively.

The equilibrium condition is thus fulfilled for each acid after the mixing, since e. g. for the first

$$C_H \times C_H \frac{V_1}{V_1 + V_2} : C_{Z_1H} \frac{V_1}{V_1 + V_2} = C_H^2 : C_{Z_1H} = K_1.$$

Applying this to the above case, we have

$$C_{Z_1H} + C_H = \frac{1}{3.208}, \text{ whence from (1) } C_H = 0.00236;$$

$$C_{Z_2H} + C_H = \frac{1}{240.6}, \text{ whence from (2) } C_H = 0.00249.$$

The two solutions are therefore not isohydric, and a displacement of equilibrium will occur, producing an effect on the conductivity which may be calculated, and tested for the case of equal volumes of each component. The total concentration of the acids is then

$$Z_1 = C_{Z_1H} + C_{Z_1} = \frac{1}{6.416} \quad Z_2 = C_{Z_2H} + C_{Z_2} = \frac{1}{481.2},$$

and the molecular conductivity of the mixture is

$$\frac{\mu'_{\infty} C_{Z_1} + \mu''_{\infty} C_{Z_2}}{Z_1 + Z_2},$$

in which  $\mu'_{\infty} = 364$  and  $\mu''_{\infty} = 362$ .

We come then to the calculation of  $C_{Z_1} = x$  and  $C_{Z_2} = y$  by the equations

$$\frac{C_{Z_1} C_{H}}{C_{Z_1 H}} = 0.000018 \quad \frac{C_{Z_2} C_{H}}{C_{Z_2 H}} = 0.0037,$$

in which

$$C_H = C_{Z_1} + C_{Z_2}, \quad C_{Z_1 H} = Z_1 - C_{Z_1} \text{ and } C_{Z_2 H} = Z_2 - C_{Z_2};$$

hence

$$\frac{C_{Z_1}(C_{Z_1} + C_{Z_2})}{Z_1 - C_{Z_1}} = 0.000018 \quad \frac{C_{Z_2}(C_{Z_1} + C_{Z_2})}{Z_2 - C_{Z_2}} = 0.0037,$$

which give

$$\frac{x(x+y)}{0.156-x} = 0.000018 \text{ and } \frac{y(x+y)}{0.00208-y} = 0.0037.$$

The direct solution of these equations is impossible, but it can be arrived at by successive approximation, the value of  $y$  found with assumed values of  $x$  from the first equation

$$y = \frac{0.000018(0.156-x)}{x} - x,$$

being substituted in the second. The molecular conductivity is found in this way to be 5.56, while experiment gave 5.51.

(g) *Equilibrium in solutions of electrolytes, discussed theoretically.* Whilst for half-electrolytes Ostwald's law of dilution supplies a basis for theoretical treatment, that starting-point fails in the case of strong acids and bases, as well as salts. Only an empirical formula<sup>1</sup> has been obtained, which expresses with fair accuracy the change of molecular conductivity with the concentration

$$\frac{C_j^n}{C_a^2} = K,$$

<sup>1</sup> Rudolphi, *Zeitschr. f. Phys. Chem.* 17. 385; Van 't Hoff, l. c. 18. 301; Kohlrausch, l. c. 18. 661.

instead of Ostwald's law

$$\frac{C_j^2}{C_s} = K,$$

in which  $C_j$  and  $C_s$  are the concentrations of the ions and of the undissociated part.

The following series of observations on silver nitrate at  $25^\circ$  will serve as illustration :—

$V$ (volume in litres per gram-molecule).	$\frac{\mu}{\mu_\infty}$	$K = \frac{\mu^3}{\mu_\infty (\mu_\infty - \mu)^2 V}$
16	0.8283	1.11
32	0.8748	1.16
64	0.8993	1.06
128	0.9262	1.07
256	0.9467	1.08
512	0.9619	1.09

This relation holds in many cases, and although as yet no theoretical basis for it is known, it is conceivably capable of further extension, and it seems most suitable to make use of the degree of dissociation simply, as expressed by the value of  $i$ ; i.e. the ratio in which the number of molecules is increased by the dissociation. That ratio may be determined in several ways, most simply by the freezing point, in which it appears as the quotient of the observed molecular depression by its normal value 18.7. From the conductivity it may be derived, as already explained, by means of  $\frac{\mu}{\mu_\infty}$ , only that for polyionic molecules we must put

$$i = 1 - \frac{\mu}{\mu_\infty} + a \frac{\mu}{\mu_\infty} = 1 + (a - 1) \frac{\mu}{\mu_\infty},$$

where  $a$  is the number of ions, 2 for  $\text{KCl}$ , 3 for  $\text{CaN}_2\text{O}_6$ , 5 for  $\text{K}_4\text{FeCy}_6$ , &c. Finally, the osmotic pressure is increased  $i$  times in accordance with the application of Avogadro's law to solutions.

The following table shows the agreement between the results of these three methods :—

	Normality.	$i$ (freezing point) <sup>1</sup> .	$i$ (conductivity) <sup>2</sup> .	$i$ (osmotic pressure, <sup>3</sup> .
KCl	0.14	1.82	1.86 (1.85)	1.81
NH <sub>4</sub> Cl	0.148	1.83	1.89 (1.84)	1.82
LiCl	0.13	1.94	1.84 (1.79)	1.92
MgSO <sub>4</sub>	0.38	1.2	1.35 (1.35)	1.25 (1.4)
CaN <sub>2</sub> O <sub>6</sub>	0.18	2.47	2.46	2.48
SrCl <sub>2</sub>	0.18	2.52	2.51	2.69 (2.4)
MgCl <sub>2</sub>	0.19	2.68	2.48	2.79 (2.3)
CaCl <sub>2</sub>	0.184	2.67	2.42	2.78 (2.4)
K <sub>4</sub> FeCy <sub>6</sub>	0.356	—	3.07	3.09

It should be noted that the value of  $i$  may vary with the temperature as well as with the concentration.

(h) *Equilibrium in electrolytes. Applications. Indirect analysis by catalysis. Action of acetates on acetic acid.* We will again deal first with an application which, without the aid of the dissociation theory, can hardly be touched. It is observed that the inverting action of weak acids, e.g. acetic acid, is greatly diminished by presence of their salts, such as sodium acetate. The assumption that the action on cane sugar is due to the hydrogen ions—the rate of inversion is found to be proportional to the concentration of these as measured by the conductivity—enables us easily to explain the fact. The dissociation of acetic acid is reduced by addition of any of its salts, since that brings the acetyl ion  $C_2H_3O_2$  into the solution, and accordingly the concentration of the hydrogen ions is reduced. The point may be tested numerically by means of the following table, which refers to experiments made at  $54.3^\circ$ :—

Inverting Solution.		$\frac{\mu}{\mu_\infty}$	$k \cdot 10^3$ (obs.)	$k \cdot 10^3$ (calc.)
$\frac{1}{4}$ n. $C_2H_3O_2$		—	0.75	0.75
„	$+\frac{1}{8}$ n. $C_2H_3NaO_2$	0.912	0.122	0.128
„	$+\frac{1}{4}$ „	0.76	0.07	0.079
„	$+\frac{1}{2}$ „	0.739	0.04	0.04
„	$+\frac{1}{8}$ „	0.713	0.019	0.017
„	$+\frac{1}{4}$ „	0.692	0.0105	0.0088

<sup>1</sup> From freezing-point measurements by Arrhenius, *Zeitschr. f. Phys. Chem.* 1. 631; Jones, l. c. 11. 114, 12. 639; Wildermann, l. c. 19. 242.

<sup>2</sup> From the conductivity according to Kohlrausch and Van 't Hoff-Reicher, l. c. 3. 201.

<sup>3</sup> From osmotic phenomena according to De Vries, l. c. 3. 103, and Hamburger, l. c. 2. 425.

<sup>4</sup> Arrhenius, l. c. 5. 7.



Let us start from the rate of inversion by  $\frac{1}{80}$  normal HCl at  $54.3^\circ$ ; it is

$$k = 4.69 \times 10^{-3} \text{ (per minute),}$$

i.e. 4.69 parts in a thousand of the cane sugar present are inverted in a minute, by H-ions of concentration  $\frac{1}{80}$  normal; for hydrochloric acid of that diluteness may be taken as completely dissociated.

The concentration of the H-ions,  $C_H$ , in  $\frac{1}{4}$  normal acetic acid may be calculated from the equation of equilibrium:

$$\frac{C_H}{C_{C_2H_4O_2}} = 1.615 \times 10^{-5},$$

in which  $C_{C_2H_4O_2} = \frac{1}{4} - C_H$ , whence  $C_H = 0.002$ . The velocity should be accordingly:

$$\frac{1}{80} : 0.002 = 4.69 \times 10^{-3} : k$$

$$k = 0.75 \times 10^{-3}$$

in complete agreement with the observed value, which shows that the rate of inversion is in proportion to the concentration of the H-ions.

On addition of sodium acetate of normality  $n$ ,  $C_2H_3O_2^-$  ions are brought into the solution, of concentration  $= n \frac{\mu}{\mu_\infty}$ ,

in which  $\frac{\mu}{\mu_\infty}$ , obtainable from the conductivity, expresses the fraction of the salt dissociated. The equation of equilibrium is now

$$\frac{\left(n \frac{\mu}{\mu_\infty} + C_H\right) C_H}{\frac{1}{4} - C_H} = 1.615 \times 10^{-5},$$

from which the values of  $k$  above are calculated by means of

$$\frac{1}{80} : C_H = 4.69 \times 10^{-3} : k.$$

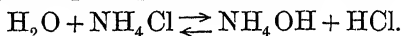
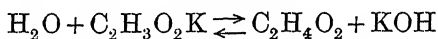
The agreement is very good, and may suffer a slight correction, at high concentrations, on account of the influence which addition of salt appears to have even when no dis-

placement of equilibrium occurs. The velocity of inversion is raised, independently of the nature of the salt, and proportionally to the amount of it, by 6.3 per cent. for 0.1 normality, so that the last number 0.0088 is to be increased by  $6.3 \times 2.5 = 15.75\%$ , and becomes 0.0102 against the observed value 0.0105.

(i) *Equilibrium in electrolytes. Applications. Hydrolysis.* Hydrolysis, so called, i.e. decomposition of salts by solution in water, is highly important, since it occurs so often. According as we are concerned with strong or weak acids or bases, four combinations are possible, of which one—the case of a strong acid with a strong base—may be left out, since the hydrolysis is then, under ordinary conditions, too small to observe.

We have then, on the one hand, cases in which either a weak acid or a weak base takes part in the formation of the salt; on the other, that in which both acid and base are weak.

(a) *Hydrolysis of salts of weak bases and strong acids.* When a salt of a weak acid, such as acetic, or a weak base, such as ammonia, is dissolved in water, equilibrium occurs according to one of these equations:



A certain amount of acid or of base becomes free, and determined in any manner, will serve as measure of the hydrolysis. Dibbitts, e.g., distilled solutions of acetates, and determined how strong a solution of acetic acid must be to give a distillate of the same character.

Walker<sup>1</sup> attacked the problem more generally by bringing acid and base together in various proportions, not only equivalent, and then determined the fraction remaining uncombined. In the cases chosen by him, a weak base and a strong acid were used—e.g. urea and hydrochloric acid—and the quantity of free acid present was found by a

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 4. 319.

measurement of the rate of inversion, or of conductivity. The leading result was this relation :

$$\frac{C_{acid} C_{base}}{C_{salt}} = \text{const.} \quad (1)$$

where  $C_{acid}$ ,  $C_{base}$ ,  $C_{salt}$ , mean respectively the concentration of the acid, the base, and the salt. This appears from the following table for the rate of inversion  $k$ :—

Normal hydrochloric acid at 25°.

Gram-molecules of urea per litre.	$k$	Constant from (1).
0	0.00315 ( $k_0$ )	—
$\frac{1}{2}$	237	0.767
1	184	0.818
2	114	0.721
3	082	0.795
4	060	0.751

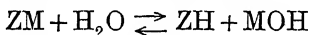
The constant is calculated in the following way:—

$\frac{k}{k_0}$  is the fraction of acid remaining free, therefore  $1 - \frac{k}{k_0}$  is combined part, i.e. the salt, and the free base is accordingly  $n - 1 + \frac{k}{k_0}$ . Hence equation (1) becomes

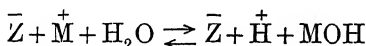
$$\frac{\frac{k}{k_0} \left( n - 1 + \frac{k}{k_0} \right)}{1 - \frac{k}{k_0}} = \text{const.}$$

The relation so proved is actually that which is to be expected from the dissociation theory.

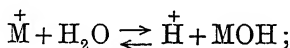
The general equation of hydrolysis



takes, on account of the almost complete ionization of the salt and the strong acid, while the base remains practically undissociated, the form



or



hence from

$$\Sigma n \log C = \text{const.}$$

it follows that

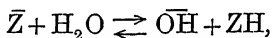
$$\log C_H + \log C_{MOH} - \log C_M = \text{const.}$$

or

$$\frac{C_H C_{MOH}}{C_M} = \text{const.},$$

in complete agreement with (1), since  $C_H$  is the concentration of the acid,  $C_{MOH}$  of the base, and  $C_M$  of the salt<sup>1</sup>.

(β) *Hydrolysis of salts of strong bases and weak acids.* The deduction just made may be applied to this case also, and leads, on the assumption of complete dissociation of the salt and base, and inconsiderable dissociation of the acid, to the equation



whence

$$\frac{C_{OH} C_{ZH}}{C_Z} = \text{const.},$$

which comes to the same relation as in the hydrolysis of salts of weak bases:

$$\frac{C_{base} C_{acid}}{C_{salt}} = \text{const.}$$

The hydrolysis in this case, of which potassium cyanide may serve as example, was measured by the saponifying action of the free alkali<sup>2</sup>. It is known that the velocity of reaction is conditioned by

$$-\frac{dC}{dt} = kCC_{base},$$

where  $C_{base}$  stands for the concentration of the base (KOH), and  $C$  for that of the ester (ethyl-acetate), and  $k=6.22$  ( $t$  in minutes) at  $24.2^\circ$ . If then the rate of saponification

—  $\frac{dC}{dt}$  is measured for a known concentration of the ester,

<sup>1</sup> Shields, *Zeitschr. f. Phys. Chem.* 12. 167.

<sup>2</sup> [The concentration of the water is practically unaltered by the reaction, on account of the great mass of it present, so that the factor  $C_{H_2O}$  may be omitted from the equation.—TRANSLATOR.]

the concentration of the free base may be calculated. The calculation is, however, complicated by the fact that this is not a catalytic action, but one in which the quantity of active alkali is reduced. That would not be the case if, e.g., the catalytic conversion of hyoscyamine into atropine by bases were chosen. Nevertheless the following data were obtained:—

Normality ( $C_{\text{KCN}}$ )	Percentage hydrolyzed ( $p$ )	$p^2 C_{\text{KCN}} 10^4$
0.9474	0.31	0.9 $\times 10^{-5}$
0.2348	0.72	1.22 „
0.0952	1.12	1.16 „
0.0238	2.34	1.3 „

The measurements agree with the equation

$$\frac{C_{\text{base}} \times C_{\text{acid}}}{C_{\text{salt}}} = \text{const.},$$

in which, for this special case,

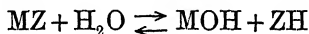
$$C_{\text{base}} = C_{\text{acid}} = \frac{p}{100} C_{\text{KCN}},$$

so that

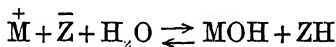
$$\left( \frac{p}{100} C_{\text{KCN}} \right)^2 : C_{\text{KCN}} = p^2 C_{\text{KCN}} 10^{-4} = \text{const.}$$

( $\gamma$ ) *Hydrolysis of salts of weak acids and weak bases.* For the sake of completeness we must consider also the case in which both acid and base are weak. The former rule no longer holds, but in a limiting case it may be replaced by another, also easily arrived at.

The limiting case in question is where the salt is completely dissociated, but the acid and base hardly at all; then the equation



becomes



and we obtain

$$\frac{C_{\text{MOH}} C_{\text{ZH}}}{C_{\text{M}} C_{\text{Z}}} = \text{const.},$$

i. e.

$$\frac{C_{base} C_{acid}}{C_{salt}^2} = \text{const.}$$

The essential difference is, therefore, that the concentration of the salt enters as the second power instead of the first.

In this case, therefore, unlike the other, the hydrolysis is independent of the dilution.

The following table contains data for aniline-acetate, which confirm this result<sup>1</sup>. The hydrolyzed fraction, as determined by the conductivity, is given under *s*, while *V* is the volume in litres containing one gram-molecule of aniline-acetate:

<i>V</i>	12.5	25	50	100	200	400	800
<i>s</i>	0.454	0.442	0.436	0.449	0.444	0.446	0.431

The constancy of *s* is in agreement with the above formula.

Before going further with the calculations in this connexion, we will consider a chief factor in the phenomena of hydrolysis—the dissociation of water itself.

(δ) *Electrolytic dissociation of water and hydrolysis.* If one is not previously convinced of the correctness of the electrolytic dissociation theory, hardly any result won by means of it is so convincing as the agreement between the conclusions drawn in completely different ways as to the degree of dissociation of water itself.

Ostwald<sup>2</sup> calculated it at  $1 \times 10^{-7}$  at 25° on the basis of a measurement of the electromotive force of an oxygen-hydrogen battery; i. e. in a litre  $1 \times 10^{-7}$  gram-molecule would be present as the ions  $\text{H}^+$  and  $\text{OH}^-$ .

Arrhenius<sup>3</sup> arrived at the value  $1.1 \times 10^{-7}$  from Shields' measurements of the hydrolysis of salts.

<sup>1</sup> Arrhenius-Walker, *Zeitschr. f. Phys. Chem.* 5, 20.

<sup>2</sup> *Ber. d. kgl. sächs. Ges. d. Wiss.*, Jan. 93; *Zeitschr. f. Phys. Chem.* 11, 521; Nernst, l. c. 14, 155.

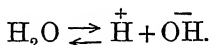
<sup>3</sup> *Ber. d. kgl. schwed. Akad. d. Wiss.*, Feb. 93; *Zeitschr. f. Phys. Chem.* 11, 827; Bredig, l. c. 11, 829.

Wys<sup>1</sup> concluded  $1.2 \times 10^{-7}$  from the velocity of esterification in pure water.

Kohlrausch and Heydwiller<sup>2</sup> obtained  $1.05 \times 10^{-7}$  from the conductivity of the purest water.

After such an agreement, it is hardly conceivable that the basis on which all these results rest should be further altered.

The fundamental assumption<sup>3</sup> is that, in water, an equilibrium subsists between the undecomposed molecules and the ions, according to the equation:



Hydrolysis can be completely explained on that basis of assumption. If we have a salt ZM hydrolytically decomposed, there are in solution:

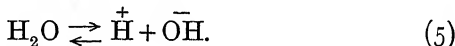
The salt ZM and its ions  $\bar{\text{Z}}$  and  $\overset{+}{\text{M}}$ ;

The base MOH, the acid ZH, water  $\text{H}_2\text{O}$ , and its ions  $\bar{\text{O}}\text{H}$  and  $\overset{+}{\text{H}}$  according to the above assumption.

Besides the main equilibrium between the undissociated molecules



the following equilibria occur:—



Each of these equilibria leads to a relation, which, however, is not in all cases known.

From (1) we have immediately

$$\frac{C_{\text{ZH}} C_{\text{MOH}}}{C_{\text{MZ}}} = K_1,$$

and from (5)

$$C_{\text{H}} C_{\text{OH}} = K,$$

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 11. 492 (March, 1893), 12. 514; Van Laar, l. c. 13. 736.

<sup>2</sup> *Sitz.-Ber. d. kgl. preuss. Akad. d. Wiss.*, March, 1894; *Zeitschr. f. Phys. Chem.* 14. 317; Tower, l. c. 18. 47.

<sup>3</sup> Arrhenius, l. c. 5. 16.

which constant, from the preceding data for pure water

$$C_H = C_{OH} = 1.09 \times 10^{-7},$$

is found to be

$$K = 1.09^2 \times 10^{-14} = 1.2 \times 10^{-14}.$$

The relations resulting from (2) and (3) are known for the case of weak acids and bases :

$$\frac{C_Z C_H}{C_{ZH}} = K_2 \dots (2) \quad \text{and} \quad \frac{C_M C_{OH}}{C_{MOH}} = K_3 \dots (3).$$

It may be remarked in passing that when both acid and base follow the dissociation law, i.e. when they are both weak, the salt formed from them necessarily obeys it too, according to the above relations<sup>1</sup>—for

$$\frac{(1) \times (2) \times (3)}{(5)} \text{ gives } \frac{C_Z C_M}{C_{ZM}} = \frac{K_1 K_2 K_3}{K_5} = \text{const.}$$

Important conclusions as to hydrolysis itself may be drawn from the dissociation of water, conclusions that take a very simple form for the limiting case of complete dissociation of the salt, and, if either base or acid is strong, complete dissociation of that too.

If the salt is formed from a strong base and weak acid we may assume that the free acid is practically undissociated, the base dissociated. Then from the relations

$$\frac{C_Z C_H}{C_{ZH}} = K_2 \quad C_H C_{OH} = K$$

we get

$$\frac{C_{OH} C_{ZH}}{C_Z} = \frac{K}{K_2},$$

in which  $C_{OH}$  represents the dissociated, i.e. approximately the free base, and  $C_{ZH}$  the free acid, the latter undissociated;  $C_Z$  is the quantity of acid which is not in the free state, consequently in the form of salt; in other words, it expresses the quantity of salt.

The former relation (p. 129)

$$\frac{C_{base} C_{acid}}{C_{salt}} = \text{const.}$$

<sup>1</sup> The determinations for, e.g., aniline acetate (*Zeitschr. f. Phys. Chem.* 5. 16) are, however, not favourable to this view.



is consequently recovered, but with the advantage that the constant in question may now be calculated, being the quotient of the dissociation constant of water by that of the acid. The correctness of this deduction may be tested.

According to Shields' <sup>1</sup> determinations by the rate of saponification, 0.0952 normal sodium acetate solution at 25° is hydrolyzed to the extent of 0.008 %, so that

$$C_{acid} = C_{base} = 0.00008 \times 0.0952$$

$$C_{salt} = 0.0952 (1 - 0.00008) = 0.0952,$$

and the constant of hydrolysis

$$\frac{(0.00008 \times 0.0952)^2}{0.0952} = 0.00008^2 \times 0.0952 = 0.61 \times 10^{-9} = \frac{K}{K_2}.$$

The dissociation constant of water is however  $1.2 \times 10^{-14}$ , and that of acetic acid, all at 25°,  $K_2 = 1.81 \times 10^{-5}$ ; hence

$$\frac{K}{K_2} = \frac{1.2}{1.81} \times 10^{-9} = 0.66 \times 10^{-9}.$$

These data and calculations are, however, still somewhat uncertain <sup>2</sup>.

In just the same way as for the salt of a weak acid, in the relation

$$\frac{C_{acid} C_{base}}{C_{salt}} = \text{const.},$$

the constant in question is the quotient of the dissociation constant  $K$  for water by that of the acid  $K_2$ , so for the salt of a weak base such as ammonia, on account of the relations

$$\frac{C_M C_{OH}}{C_{MOH}} = K_3 \quad \text{and} \quad C_H C_{OH} = K,$$

we obtain

$$\frac{C_{base} C_{acid}}{C_{salt}} = \frac{C_{MOH} C_H}{C_M} = \frac{K}{K_3},$$

in which  $K_3$  is the dissociation constant of the base <sup>3</sup>.

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 12. 184.

<sup>2</sup> Van Laar, l. c. 12. 747; Morgan, l. c. 17. 530.

<sup>3</sup> Bredig, l. c. 11. 829, 13. 322.

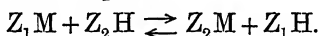
Finally, for salts like aniline acetate (p. 130), with both acid and base weak,

$$\frac{C_M C_{OH}}{C_{MOH}} = K_3, \quad \frac{C_Z C_H}{C_{ZH}} = K_2, \quad C_H C_{OH} = K,$$

and therefore

$$\frac{C_{base} C_{acid}}{C_{salt}^2} = \frac{C_{MOH} C_{ZH}}{C_M C_Z} = \frac{K}{K_2 K_3}.$$

(k) *Avidity.* Hydrolysis forms an intermediate step to a second mode of decomposition of salts. The action of water in hydrolysis may be regarded as that of a very weak acid, or base, which partly displaces the weak acid, or base, of the dissolved salt. This case therefore leads to others in which the addition of any other acid or base to the salt leads to a similar, but more extensive decomposition. If we choose addition of an acid, then if  $Z_1 M$  is the original salt and  $Z_2 H$  the acid added, two salts are present in the solution together with the uncombined portions of the acids, according to the equation



If the ionization be taken into account we have new equilibria, each with its corresponding equation necessary to the calculation.

Two methods are available for the solution of the problems thus arising, which may be followed out in a definite and somewhat simplified experimental case.

Suppose  $a$  and  $b$  gram-molecules respectively of two weak acids  $Z_1 H$  and  $Z_2 H$ , which therefore obey Ostwald's law of dissociation (first simplification); and to them added  $c$  gram-molecules of a strong base  $MOH$ , insufficient to saturate both acids. Let the volume of the entire solution be  $V$  litres, and as second simplification let it be assumed that the salts formed are completely dissociated. Without regard to dissociation we have

$x$	gram-molecules of the salt	.	.	$Z_1 M$
$c - x$	„ „ „	.	.	$Z_2 M$
$a - x$	„ „ acid	.	.	$Z_1 H$
$b - c + x$	„ „ „	.	.	$Z_2 H$

Taking account of ionization we have to assume in the solution

Compounds	.	.	.	.	$Z_1H$ and $Z_2H$
Ions	.	.	.	.	$Z_1, Z_2, M,$ and $H$

whose relative masses are determined by the following equations:—

$$\frac{C_{Z_1}C_H}{C_{Z_1H}} = K_1, \quad \frac{C_{Z_2}C_H}{C_{Z_2H}} = K_2, \quad C_{Z_1H} + C_{Z_1} = \frac{a}{V},$$

$$C_{Z_2H} + C_{Z_2} = \frac{b}{V}, \quad C_{Z_1} + C_{Z_2} = C_M + C_H = \frac{c}{V} + C_H,$$

six equations which allow of the calculation of the six unknowns, and hence of the properties of the solution. The rate of inversion, for example, may be calculated from  $C_H$ ; the conductivity from  $C_H, C_M, C_{Z_1}$ , and  $C_{Z_2}$ ; the freezing point from the sum of all the concentrations.

Finally, the composition of the solution may be pictured with the aid of Fig. 46, in which again the equality

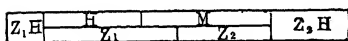


FIG. 46.

between the sum of the positive and negative ions is represented. Such a mode of treatment does not, however, answer to the usual

conception of the solution as containing the two acids partly free, and partly in the state of salts.

The second treatment of the problem supplies this defect.

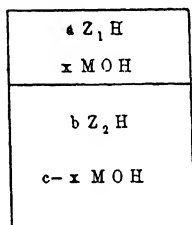


FIG. 47.

The solution is imagined divided into two parts of volume  $V_1$  and  $V_2$ ; on the one side is the acid  $Z_1H$ , on the other that  $Z_2H$ , and the base is divided between the two in such a way that two isohydric solutions are obtained—solutions, that is, in which the concentration of the hydrogen ions  $C_H$  is the same. According to p. 121 the equilibrium of the two solutions is not upset

by mixing them, and the base is divided between the two acids in the same proportion after the mixture as before.

We have now the following relations:—

In  $V_1$  are present:  $xMZ_1$  as M and  $Z_1$ ,  $(a-x) Z_1H$ , of which  $V_1C_H$  is as H and  $Z_1$ , therefore

$$C_H \frac{V_1C_H + x}{V_1} : \frac{a-x-V_1C_H}{V_1} = \frac{C_H(V_1C_H + x)}{a-x-V_1C_H} = K_1,$$

In  $V_2$  are present:  $(c-x)MZ_2$  as M and  $Z_2$ ,  $(b-c+x) Z_2H$ , of which  $V_2C_H$  is as H and  $Z_2$ , thus:

$$\frac{C_H(V_2C_H + c-x)}{b-c+x-V_2C_H} = K_2$$

and 
$$K_1 : K_2 = \frac{V_1C_H + x}{a-x-V_1C_H} : \frac{V_2C_H + c-x}{b-c+x-V_2C_H},$$

which if the dissociated quantities  $V_1C_H$  and  $V_2C_H$  are small, simplifies to

$$K_1 : K_2 = \frac{x}{a-x} : \frac{c-x}{b-c+x},$$

or, since  $x = \text{salt } Z_1M$ ,  $a-x = \text{acid } Z_1H$ ,  $c-x = \text{salt } Z_2M$ , and  $b-c+x = \text{acid } Z_2H$

$$\frac{\text{salt } Z_1M \times \text{acid } Z_2H}{\text{salt } Z_2M \times \text{acid } Z_1H} = \frac{K_1}{K_2} = \text{const.},$$

in agreement with Guldberg and Waage's law, with the further point that the constant may be calculated as the quotient of the dissociation constants of the two acids.

If we have the simple ratios of masses that occur in the experiment, when both acids and base are taken in molecular quantities, then

$$a = b = c = 1 \text{ and } K_1 : K_2 = x^2 : (1-x)^2;$$

in words, the ratio of sharing of the base between the two acids  $Z_1H$  and  $Z_2H$  ( $x : 1-x$ ) is equal to the square root of the quotient of their respective dissociation constants ( $\sqrt{K_1} : \sqrt{K_2}$ ), and that function of the constants is a measure for the so-called avidity of the acids.

It may be noted that this relation can be derived at once from the fundamental equations

$$\frac{C_{Z_1}C_H}{C_{Z_1H}} = K_1 \text{ and } \frac{C_{Z_2}C_H}{C_{Z_2H}} = K_2$$

without making use of the conception of isohydric solutions. If, as before, we neglect the hydrogen ions by comparison with the quantity of undissociated acid, then

$$C_{Z_1} = \text{salt } Z_1M, \quad C_{Z_1H} = \text{acid } Z_1H, \quad C_{Z_2} = \text{salt } Z_2M, \\ C_{Z_2H} = \text{acid } Z_2H,$$

and the quotient of the two equations gives immediately

$$\frac{K_1}{K_2} = \frac{\text{salt } Z_1M \times \text{acid } Z_2H}{\text{salt } Z_2M \times \text{acid } Z_1H}.$$

The conclusion may be proved, amongst other ways, by volume-chemical measurements of avidity<sup>1</sup>. The following data will serve at once as an example, and as an explanation of the method adopted. The latter depends on measurements of specific gravity, and gave as volume of a kilogram of the following solutions at 25°:

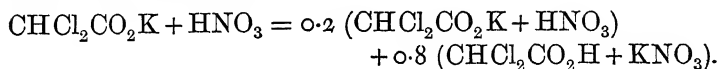
	<i>cub. cm.</i>
Solution containing 1 gram-molecule KOH . . .	950.668
"    "    "    HNO <sub>3</sub> . . .	966.623
sum	1917.291
observed	1937.337
increase of volume on neutralization . . .	20.046
Solution containing 1 gram-molecule of KOH . . .	950.668
"    "    "    CHCl <sub>2</sub> CO <sub>2</sub> H . . .	947.377
sum	1898.045
observed	1910.991
increase of solution on neutralization . . .	12.946

Complete conversion of nitric acid and potassium dichloracetate into potassium nitrate and dichloracetic acid would therefore be accompanied by an increase of volume of 20.046 - 12.946 = 7.100. The actual change of volume is given by a third experiment:

	<i>cub. cm.</i>
2 kilograms solution containing 1 gram-mol. CHCl <sub>2</sub> CO <sub>2</sub> K	1910.991
1 " " " " HNO <sub>3</sub>	966.623
	2877.614
after mixture observed . . .	2883.285
expansion . . .	5.671

<sup>1</sup> Ostwald, *Journ. f. Prakt. Chem.* 16. 396.

therefore  $5.671 \div 7.1 = 0.8$  of the whole was transformed, according to the equation



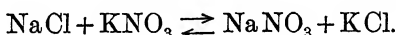
The ratio of sharing, or relative avidity, is therefore

nitric acid : dichloroacetic acid =  $0.8 : 0.2 = 4 : 1$ .

The following table<sup>1</sup> gives the fraction  $x$  (0.8 in the preceding example) of base which falls to the share of the first of the two acids, and side by side with it the value calculated from the relation  $x : 1 - x = \sqrt{K_1} : \sqrt{K_2}$ , in which  $K_1 = 0.0214$ .

			$K_2$	$x$ (obs.)	$x$ (calc.)
Formic acid :	lactic acid		0.0138	0.54	0.56
„	acetic „		0.018	0.76	0.75
„	butyric „		0.00149	0.8	0.79
„	isobutyric „		0.00144	0.81	0.79
„	propionic „		0.00134	0.79	0.8

(l) *Double decomposition.* When two salts not possessing a common ion, e.g. NaCl and KNO<sub>3</sub>, are mixed in solution, a reaction may take place, which is known as a double decomposition, and, according to the usual conceptions, leads to an equilibrium of the following form:—



Introducing the notion of ionization we have first to take the case of almost complete dissociation. We are then concerned with salts of strong acids and bases as in the above example, and no interchange takes place, but rather the solution contains the ions that were previously present in the unmixed salt solutions:  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{NO}_3^-$ .

If either the acid or the base is weak, we get a salt whose conditions of dissociation have not yet been sufficiently cleared up, and it is only when both acid and base are weak, and follow the law of dissociation, that our information is satisfactory. When acid and base both follow

<sup>1</sup> Arrhenius, *Zeitschr. f. Phys. Chem.* 5. 14.

the law of dissociation, the salt does too, according to p. 133, and we may, with Arrhenius<sup>1</sup>, carry the law of isohydric solutions further. Possible hydrolytic dissociation is here neglected.

We will suppose the mixed salt solution produced from the four solutions of the salts  $Z_1M_1$ ,  $Z_1M_2$ ,  $Z_2M_2$ ,  $Z_2M_1$ , in such quantity and dilution that no displacement of equilibrium occurs when they are mixed. For this, the first condition is that the volumes  $a, b, c, d$  must be chosen so that  $ac = bd$ , which is the case in Fig. 48, since  $a = op \times oq$ ,  $c = or \times os$ ,  $b = oq \times or$ ,  $d = op \times os$ .

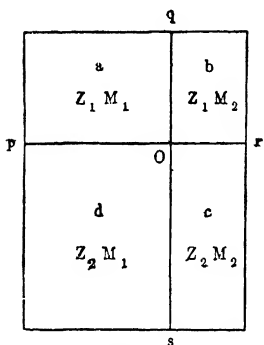


FIG. 48.

The second condition, that no displacement of equilibrium may occur on mixture, is, as previously shown (p. 121), that the concentration of the ions must be equal, i. e.

$$C_{Z_1} = C_{M_1} = C_{Z_2} = C_{M_2} = C.$$

For proof of this law, let the undissociated quantities in  $a, b, c, d$  be  $x, y, z, v$ . In  $a$  then we have, besides  $xZ_1M_1$ ,  $aCZ_1$  and  $aCM_1$ , therefore  $\frac{x}{aC^2} = k_a$  or  $x = k_a aC^2$ .

If on mixture everything remains unchanged, then the concentration of  $Z_1M_1$  becomes  $\frac{x}{a+b+c+d}$  instead of  $\frac{x}{a}$ ,

$$\text{of } M_1 \text{ is now } C \times \frac{a+d}{a+b+c+d},$$

$$\text{of } Z_1 \text{ is now } C \times \frac{a+b}{a+b+c+d}.$$

Hence the equilibrium condition

$$\frac{x}{a+b+c+d} = k_a C^2 \frac{(a+d)(a+b)}{(a+b+c+d)^2}$$

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 2. 293.

is fulfilled, since

$$(a+d)(a+b) = a^2 + ab + ad + bd = a^2 + ab + ad + ac \\ = a(a+b+c+d)$$

so that the condition reduces to  $x = k_a a C^2$ , which is fulfilled.

Now from the two conditions for isohdry

$$ac = bd \text{ and } C_{Z_1} = C_{Z_2} = C_{M_1} = C_{M_2}$$

a conclusion may be drawn which has a simple physical meaning:

$$(aC_{Z_1})(cC_{M_2}) = (bC_{Z_2})(dC_{M_1}),$$

in which

$aC_{Z_1}$	is the dissociated part of the salt	$Z_1M_1$	
$cC_{M_2}$	"	"	$Z_2M_2$
$bC_{Z_2}$	"	"	$Z_1M_2$
$dC_{M_1}$	"	"	$Z_2M_1$

i. e. the products of the dissociated parts of reciprocal pairs of salts are equal.

## 2. Influence of Temperature on Homogeneous Equilibrium.

(a) *Gases, discussed theoretically.* The simple result as to the influence of temperature on chemical equilibrium obtained by application of thermo-dynamics is that only the constant which regulates the phenomena of equilibrium at constant temperature, as explained above, is affected by change of temperature. If we take the former expression for equilibrium at constant temperature

$$\Sigma n \log C = k$$

(the logarithms being natural), the temperature law takes the following form:—

$$\frac{dk}{dT} = \frac{q}{2T^2},$$

in which  $q$  is the internal heat<sup>1</sup> developed when the kilogram-molecular quantity of the second system is converted into the first.

<sup>1</sup> i. e. the heat developed when no external work is done; in other words, when the change takes place at constant volume.



To deduce this relation we must modify the cyclic process of p. 19, which referred to the simple case of isothermal conversion under constant pressure, to suit a more general case. We have again the four reversible changes which

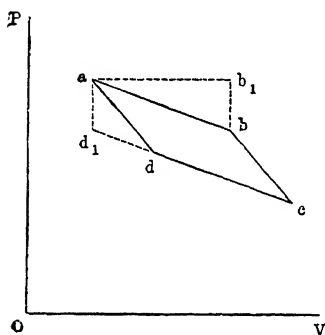


FIG. 49.

complete the cycle, corresponding to  $abcd$  (Fig. 49). Again the area of the quadrilateral represents the work done in kilogram-metres, whose magnitude, according to the second law of thermodynamics, is equal to the heat absorbed during the first isothermal process  $ab$  multiplied by  $\frac{dT}{T}$ .

The area in question is  $ab_1 \times ad_1$ , in which  $ab_1 = dV$  and  $ad_1$  the change of pressure accompanying the fall of temperature  $dT$  at constant volume, i. e.

$$ad_1 = \left( \frac{\partial P}{\partial T} \right)_V dT.$$

Finally, the heat which must be absorbed at constant temperature  $T$  in order to accomplish the expansion  $dV$  may be written

$$\left( \frac{\partial \phi}{\partial V} \right)_T dV.$$

Therefore

$$ab_1 \times ad_1 = \left( \frac{\partial P}{\partial T} \right)_V dT dV$$

in kilogram-metres, or in calories

$$A \left( \frac{\partial P}{\partial T} \right)_V dT dV,$$

so that 
$$A \left( \frac{\partial P}{\partial T} \right)_V dT dV = \left( \frac{\partial \phi}{\partial V} \right)_T dV \cdot \frac{dT}{T},$$

or 
$$A \left( \frac{\partial P}{\partial T} \right)_V = \frac{1}{T} \left( \frac{\partial \phi}{\partial V} \right)_T \quad (1)$$

Now let us suppose a reaction in the most general form

$$n_1' M_1' + n_1'' M_1'' + \dots = n_2' M_2' + n_2'' M_2'' + \dots,$$

in which  $n$  represents the number of molecules, and  $M$  the molecular formula, while the suffix 1 refers to the first system, 2 to the second. If on equilibrium  $x$  out of the kilogram-molecular quantity of the first system is converted, so that  $1-x$  remains, since for each kilogram-molecule

$$ApV = 2T,$$

in which  $p$  is the partial pressure, then altogether

$$APV = 2 [n_1(1-x) + n_2x] T \quad (2)$$

in which  $P$  is the total pressure, whilst

$$n_1 = n_1' + n_1'' + \dots \quad n_2 = n_2' + n_2'' + \dots$$

A third consideration brings  $\left(\frac{\partial \phi}{\partial V}\right)_T dV$  into relation with

the heat  $q$  which would be developed when no work is done, if the kilogram-molecular quantity of the first system is formed from the second. We have first to subtract the heat  $APdV$ , equivalent to the external work, from

$\left(\frac{\partial \phi}{\partial V}\right)_T dV$ ; the remainder corresponds to  $q$  for the quantity

$\left(\frac{\partial x}{\partial V}\right)_T dV$  which is converted when the volume increases

by  $dV$ , so that

$$q \left(\frac{\partial x}{\partial V}\right)_T dV = \left(\frac{\partial \phi}{\partial V}\right)_T dV - APdV$$

or

$$q \left(\frac{\partial x}{\partial V}\right)_T = \left(\frac{\partial \phi}{\partial V}\right)_T - AP \quad (3)$$

The relation between  $x$  and  $V$  finally is given by

$$\Sigma n \log C = k,$$

which becomes

$$\Sigma n_2 \log \frac{1-x}{V} - \Sigma n_1 \log \frac{x}{V} = k \quad (4)$$

Substituting, we get from (2)

$$A \left( \frac{\partial P}{\partial T} \right)_V = \frac{2}{V} [n_1(1-x) + n_2x] + \frac{2T}{V} (n_2 - n_1) \left( \frac{\partial x}{\partial T} \right)_V,$$

and from (3)

$$\begin{aligned} \frac{1}{T} \left( \frac{\partial \phi}{\partial V} \right)_T &= \frac{q}{T} \left( \frac{\partial x}{\partial V} \right)_T + \frac{AP}{T} \\ &= \frac{q}{T} \left( \frac{\partial x}{\partial V} \right)_T + \frac{2}{V} [n_1(1-x) + n_2x], \end{aligned}$$

and from these in the fundamental equation (1)

$$\frac{2T}{V} (n_2 - n_1) \left( \frac{\partial x}{\partial T} \right)_V = \frac{q}{T} \left( \frac{\partial x}{\partial V} \right)_T,$$

in which, according to (4), using natural logarithms:

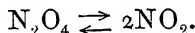
$$\left( \frac{n_2}{1-x} - \frac{n_1}{x} \right) \left( \frac{\partial x}{\partial T} \right)_V = \frac{dk}{dT} \quad \text{and}$$

$$\left( \frac{n_2}{1-x} - \frac{n_1}{x} \right) \left( \frac{dx}{dV} \right)_T = \frac{n_2 - n_1}{V},$$

i. e.

$$\frac{dk}{dT} = \frac{q}{2T^2}.$$

(b) *Gases. Applications. Nitric peroxide.* As an application of this equation, let us take the equilibrium, previously considered, in nitric peroxide, according to the symbol



$q$  is then the heat which would be developed when the kilogram-molecular quantity, i. e. 92 kilograms  $\text{N}_2\text{O}_4$ , was formed from  $2\text{NO}_2$  without external work being done; on the other hand,  $k$  is given by

$$\Sigma n \log C = k,$$

in which the terms relating to the first system are to be regarded as negative. Accordingly

$$\begin{aligned} k &= 2 \log C_{\text{NO}_2} - \log C_{\text{N}_2\text{O}_4} = 2 \log \frac{x}{V} - \log \frac{1-x}{V} \\ &= \log \frac{x^2}{V(1-x)}, \end{aligned}$$

in which  $x$  is the quantity converted into  $\text{NO}_2$ .

Integrating the equation, the small variation of  $q$  with temperature being neglected,

$$k_1 - k_2 = \frac{q}{2} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

or

$$\frac{q}{2} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) = \log \frac{x_1^2 (1 - x_2) V^2}{x_2^2 (1 - x_1) V_1}.$$

The fraction  $x$  transformed into  $\text{NO}_2$  is calculated according to p. 112 from the density  $D$  referred to air, by means of the equation

$$x = \frac{3.179}{D} - 1,$$

whilst  $V$  is given by the formula

$$APV = 2(1 + x)T;$$

and since in the experiments to be dealt with the pressure was constantly that of the atmosphere,

$$V_2 : V_1 = (1 + x_2) T_2 : (1 + x_1) T_1,$$

accordingly

$$\frac{q}{2} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) = \log \frac{x_1^2 (1 - x_2) T_2}{x_2^2 (1 - x_1) T_1}.$$

The following table contains the necessary experimental data for calculating  $q$ <sup>1</sup> :—

$$\begin{array}{ccccccc} T = 273 + 26.7 & D = 2.65 & x = 0.1996 & & q = 12900. \\ 111.3 & 1.65 & 0.9267 & & \end{array}$$

In order to test the relation found, the calculated value of  $q$  must be compared with that observed calorimetrically. The latter may be obtained approximately from the experiments of Berthelot and Ogier<sup>2</sup> on the specific heat of nitric peroxide at atmospheric pressure between 27° and 150°. In that interval of temperature 92 kilograms absorb 12,620 calories.

This quantity is composed of three parts,  $\alpha$ ,  $\beta$ , and  $\gamma$ , corresponding to the three changes effected.

<sup>1</sup> Deville and Troost, *Compt. Rend.* 64. 237.

<sup>2</sup> *Bull. de la Soc. Chim.* 37. 435.

( $\alpha$ ) Rise of temperature from  $27^\circ$  to  $150^\circ$ . The quantity required for that purpose may be calculated from the specific heat of the peroxide at high temperatures (16.86 for 92 kilograms), since then no heat is spent on dissociation; thus:

$$a = 16.86(150 - 27) = 2074.$$

( $\beta$ ) Expansion accompanies the dissociation into  $\text{NO}_2$ , and causes a conversion into external work of an amount of heat:

$$\beta = (x_2 - x_1) 2T = 577.$$

( $\gamma$ ) Conversion of  $x_2 - x_1$  kilogram-molecules of  $\text{N}_2\text{O}_4$  into  $\text{NO}_2$ :

$$q(x_2 - x_1) = 12620 - (2074 + 577),$$

whence  $q = 12500$  in good agreement with the calculated value 12900.

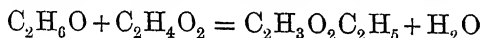
( $c$ ) *Solutions of non-electrolytes. Esterification.* The fundamental equations

$$\Sigma n \log C = k \quad \text{and} \quad \frac{dk}{dT} = \frac{q}{2T^2},$$

which have been deduced for dilute gases, are applicable also to liquids. Of these two equations, the first has been extended, on p. 113, to solutions of non-electrolytes; and, following the manner of p. 142, the second may be extended if the osmotic pressure be introduced in the proof instead of the gas pressure, and the corresponding laws of osmotic pressure be applied.

To test the result we may again compare the values of  $q$  derived from the displacement of equilibrium, and from calorimetric observation; and here a particular consequence of the theory may be noted, and verified in the study of esterification equilibrium.

According to calorimetric observations<sup>1</sup>, the reaction



is not accompanied by any measurable heat change: or

$$q = 0.$$

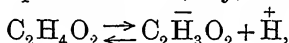
<sup>1</sup> *Bull. de la Soc. Chim.* 31. 352.

Hence  $\frac{dk}{dT} = 0$  also, i. e. the equilibrium is not upset by change of temperature, and in fact at  $10^\circ$  65.2% was converted into ester in a mixture of acetic acid and ethyl alcohol in equivalent proportions, while at  $220^\circ$  the same limit (66.5%) was found<sup>1</sup>.

(d) *Solutions of half-electrolytes.* For weak acids and bases, since Ostwald's law of dilution holds, we may make use of the thermo-dynamic formula

$$\frac{dk}{dT} = \frac{q}{2T^2}.$$

The symbol of equilibrium for, say, acetic acid,



gives us from the general equation

$$k = \Sigma n \log C$$

the particular form

$$k = \log C_{\text{H}} + \log C_{\text{C}_2\text{H}_3\text{O}_2} - \log C_{\text{C}_2\text{H}_4\text{O}_2}.$$

If a gram-molecule is contained in  $V$  litres, then

$$C_{\text{H}} = C_{\text{C}_2\text{H}_3\text{O}_2} = \frac{\mu}{V\mu_\infty} \text{ and } C_{\text{C}_2\text{H}_4\text{O}_2} = \frac{1}{V} \left(1 - \frac{\mu}{\mu_\infty}\right)$$

( $\mu$  is the molecular conductivity of the acid solution,  $\mu_\infty$  its limiting value for infinite dilution, see p. 118) and

$$k = \log \frac{\mu^2}{V\mu_\infty(\mu_\infty - \mu)} = \log K.$$

The value of  $K$  under the logarithmic sign, whose constancy at constant temperature has already been shown (p. 118), has been found to possess at  $10^\circ$  and  $40^\circ$  the (mean) values shown in the following table<sup>2</sup>. Thence  $q$  is calculated according to

$$q \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = 2 \log \frac{K_2}{K_1}.$$

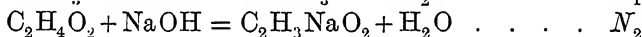
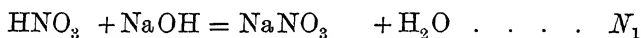
<sup>1</sup> Berthelot, *Essai de Mécanique Chimique*, 2. 73.

<sup>2</sup> Arrhenius, *Zeitschr. f. Phys. Chem.* 4. 96, 9. 339; Jahn, l. c. 16. 72; Euler, l. c. 21. 257; Baur, l. c. 23. 409.

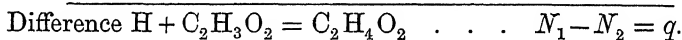
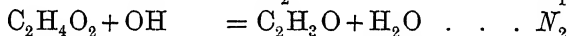
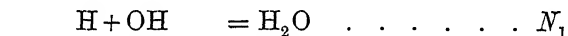
<i>Acid.</i>	$K_1(10^\circ)$	$K_2(40^\circ)$	$q$
Acetic . . .	0.0000179	0.0000187	257
Propionic . . .	138	141	126
Butyric . . .	166	162	-144

Here  $q$  is the heat that would be developed—no external work being done—if a kilogram-molecule of acid were formed in solution at  $25^\circ = \frac{10+40}{2}$  from its ions.

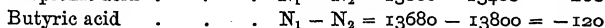
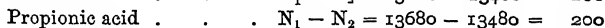
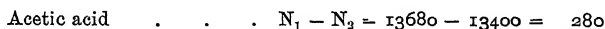
Calorimetrically this quantity may be found as the difference between the heats of neutralization  $N_1$  and  $N_2$  of dilute nitric and, say, acetic acid by a dilute strong base. For



and remembering that nitric acid and the sodium salts are almost completely dissociated, but acetic acid hardly at all, in solutions such as Thomsen used in his calorimetric researches (1 gram-molecule of acid or base in 200 gram-molecules of water), these equations may be written in the form



The values of  $N_1 - N_2$  have been found to be very small, in accordance with the preceding theory :



and have the required positive sign in the case of acetic and propionic acids, and the negative one for butyric.

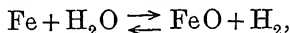
## B. Heterogeneous Equilibrium.

### 1. Relations at Constant Temperature.

(a) *In presence of gases.* The equation which served as basis for dealing with homogeneous equilibrium,

$$\Sigma n \log C = k,$$

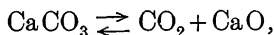
may be applied to heterogeneous equilibrium too; that is, when, in addition to (dilute) gases, solid bodies are present, as in the equilibrium between iron, iron oxide, steam, and hydrogen, according to the equation



only here a simplification is possible, for it is not necessary to include the solids under  $\Sigma n \log C$ .

This modification is permissible because the concentration of the solids considered in the gaseous mixture, in which the equilibrium is effected, has a value depending on the saturation or maximum pressure, so that the corresponding term  $n \log C$  in the above equation is unconditionally constant, and may therefore be transferred to the right-hand side. Without making the assumption here involved of the maximum pressure, we may arrive at the modified equilibrium condition by carrying out the cyclic process previously described (p. 106), supposing in it the presence of an excess of the solids Fe and FeO in the compartments A and B of Fig. 44. Then what is converted in the one sense in A is reformed in B by a conversion in the opposite sense.

The first conclusion to be drawn from the application of the fundamental equation is that when only one substance is present as gas or vapour, which is absent in the solid form, its concentration must be constant at any given temperature, i. e. its pressure must be. The phenomenon thus, by the existence of a maximum pressure, connects with that of simple evaporation; e. g. there is a maximum pressure for the partial decomposition of calcium carbonate:



in which only carbon dioxide is not present in the condensed state. So also with the maximum pressure of hydrates previously (p. 56) dealt with, in which water vapour is in the same circumstances.

If more than one gas or vapour occurs in the gaseous phase, and not condensed, the fundamental equation leads



to a relation between their concentrations; thus in the case quoted, of partial oxidation of iron, we have

$$\log C_{\text{H}_2} - \log C_{\text{H}_2\text{O}} = k \text{ or } P_{\text{H}_2} : P_{\text{H}_2\text{O}} = \text{const.}$$

Accordingly the relation between partial pressure of hydrogen and water vapour is constant, as appears from the following data<sup>1</sup> :—

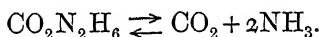
Temperature 200°.

Pressure of hydrogen, $P_{\text{H}_2}$ .	Pressure of water vapour, $P_{\text{H}_2\text{O}}$ .	$P_{\text{H}_2} : P_{\text{H}_2\text{O}}$
95.9 mm.	4.6 mm.	20.8
195.3	9.7	20.1

The same relation is observed in the equilibrium between ammonium carbonate on the one side, ammonia and carbon dioxide on the other<sup>2</sup>, the latter in varying ratios produced by intentional addition of one or other gas. We have then

$$P_{\text{CO}_2} P_{\text{NH}_3}^2 = \text{const.},$$

as may be deduced from the fundamental equation, in accordance with



(b) *In presence of solutions. Non-electrolytes.* Since scarcely any applications have been made in this region, it will be sufficient to mention briefly the rules to be expected, which may readily be done, since the fundamental equation

$$\sum n \log C = k$$

is applicable when a dilute solution is in contact with the single substances partially dissolved in it. The deduction may be made just as on p. 106, remembering the modification due to the presence of solids. The concentrations of the solids then disappear from the equation, so that the latter finally includes only such bodies as are present exclusively in the dissolved state.

(c) *In presence of solutions. Half-electrolytes.* As explained on p. 120, the addition of a half-electrolyte, e.g. acetic acid, to the solution of a second half-electrolyte, e.g. formic acid, produces a displacement of equilibrium: the quantity

<sup>1</sup> Debray, *Compt. Rend.* 88. 1341.

<sup>2</sup> Horstmann, *Ann. de Chem. u. Pharm.* 187.

of H-ions keeping equilibrium with the formic acid is increased by the H-ions dissociated from the acetic acid. The displacement may be calculated from Ostwald's law of dilution, and is verified by experiment. A similar but more obvious case is when one of the two acids is present to saturation, since then the change of equilibrium shows itself in an actual precipitation. The phenomenon may be followed out numerically when the solution is dilute enough, for which purpose the acid with which it is saturated must be a somewhat insoluble one, e.g.  $\alpha$ -bromiso cinnamic<sup>1</sup>. Its solubility (in gram-molecules per litre) at 25° is diminished by e.g. oxanilic acid (also expressed in gram-molecules per litre) in the way shown by the following table:—

Addition (A).	Solubility observed.	Solubility calculated (C).
0	0.0176	—
0.0272	0.014	0.0136
0.0524	0.0129	0.012

The alteration of equilibrium is given by the following equation:—

The dissociation constant of  $\alpha$ -bromiso cinnamic acid is 0.0144, so that in the saturated solution there is present an undissociated quantity given by  $1 - x$  in the equation

$$\frac{(0.0176x)^2}{0.0176(1-x)} = \frac{0.0176x^2}{1-x} = 0.0144 \quad 1-x = 0.416.$$

This quantity in gram-molecules per litre is  $0.0176 \times 0.416 = 0.00732$ , and represents saturation with the undissociated salt, and remains the same on addition of the oxanilic acid, only the dissociated quantity being affected.

Calling  $C$  the total concentration, we have in solution

$\alpha$ -bromiso-cinnamyl ions . . . .	$C - 0.00732$
H-ions . . . . .	$C - 0.00732$

then let the total oxanilic acid be  $A$ , of which  $a$  is dissociated:

Undissociated oxanilic acid . . . .	$A - a$
Oxanilic acid ions . . . . .	$a$
H-ions . . . . .	$a$

When both acids are present we get the equations—first,

$$\frac{(C - 0.00732)(C - 0.00732 + a)}{0.00732} = 0.0144$$

or  $(C - 0.00732)(C - 0.00732 + a) = 0.0001054$ ;  
second, since the dissociation constant of oxanilic acid is 0.0118,

$$a(C - 0.00732 + a) = 0.0118(A - a).$$

From the two equations, in which  $A$  is known,  $C$  and  $a$  unknown,  $C$  may be calculated, and is given in the third column of the preceding table.

(d) *In presence of solutions. Electrolytes.* In the case of electrolytes, i.e. of electrolytically dissociated bodies whose law of dissociation has not yet been explained, as with salts, strong acids, and bases, an exhaustive treatment is only possible when there is total dissociation into ions. The ions are then to be treated in the equations as molecules, and the fundamental equation

$$\Sigma n \log C = k$$

holds, application of which may then be made. If the ionization is incomplete, only approximate calculations can be arrived at; still they allow of a fairly close insight into the phenomena.

A method of this kind, dating from times when the electrolytic dissociation theory had not become accepted, rests on the following basis. To an electrolyte the relation

$$APV = 2T$$

is not applicable, since the osmotic pressure is abnormally high on account of the dissociation. The expression must be modified into

$$APV = 2iT,$$

where  $i$  expresses how many times the number of molecules (and consequently the pressure) is increased by dissociation. According to p. 119  $i$  may be found, amongst other ways by dividing the observed molecular depression  $t_M$  by the normal value 18.7, or

$$i = \frac{t_M}{18.7};$$

it may also be found from the conductivity (p. 124) as

$$i = 1 + (a-1) \frac{\mu}{\mu_\infty},$$

where  $a$  is the number of ions into which the molecule breaks up.

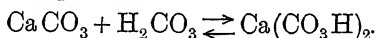
If now the above equation ( $APV = 2iT$ ) be used instead of  $APV = 2T$  in the deduction of

$$\Sigma n \log C = k,$$

and the change of  $i$  with the volume neglected, we get

$$\Sigma ni \log C = k.$$

As an example let us consider the solubility of calcium carbonate in water saturated with carbon dioxide under varying pressure ( $P$ ). In the solution there is equilibrium according to the equation



Hence, as for carbonic acid, being undissociated,  $i = 1$ , and for acid calcium carbonate from freezing-point measurements  $i = 2.56$ , we expect and find

$$\log C_{\text{H}_2\text{CO}_3} - 2.56 \log C_{\text{Ca}(\text{CO}_3\text{H})_2} = k,$$

whence

$$A = cP^{0.39},$$

where  $A$  is the quantity of lime dissolved, corresponding to  $C_{\text{Ca}(\text{CO}_3\text{H})_2}$ ,  $P$  the pressure, corresponding to  $C_{\text{H}_2\text{CO}_3}$ , and  $c$  a constant; in other words, the quantity of lime dissolved is proportional to the pressure raised to the power 0.39. Schloesing<sup>1</sup> found, in striking agreement, the same form of function with the exponent 0.37866.

The deduction of the formula on the assumption of a constant value of  $i$  is only allowable for the limiting case of extreme dilution with accompanying complete dissociation; then  $i = 3$  for acid calcium carbonate, which breaks up into the ions  $\text{Ca}$  and  $2(\text{CO}_3\text{H})$ . Hence

$$A = cP^{0.333}.$$

<sup>1</sup> *Compt. Rend.* 74. 1552, 75. 70.

So far as complete dissociation does not occur, there will be a tendency towards an exponent higher than 0.333.

## 2. Influence of Temperature on Heterogeneous Equilibrium.

(a) *Gases.* The fundamental equation arrived at for homogenous equilibrium,

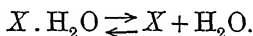
$$\frac{dk}{dT} = \frac{q}{2T^2},$$

may be applied to heterogeneous equilibrium, just as on p. 142, the constant  $k$  referring then to the expression

$$\Sigma n \log C = k,$$

in which those terms are neglected which relate to the concentration of the solid bodies present.

The sharpest test, so far, of the equation is the case of the vapour pressure of water of crystallization discussed on p. 58. There we have a salt  $X \cdot H_2O$  (e.g.  $Ba_2HPO_4 \cdot 12H_2O$ ), that decomposes into water vapour and anhydride, or a lower hydrate, and reaches equilibrium according to the equation



The condition of equilibrium at constant temperature here is simply

$$\log C_{H_2O} = k,$$

i. e. constant concentration or pressure of water vapour. For the influence of temperature we have the relation

$$\frac{d \log C_{H_2O}}{dT} = \frac{q}{2T^2}.$$

It must be noticed that this equation was given in another form on p. 59, as

$$\frac{d \log P}{dT} = \frac{q'}{2T^2},$$

with pressure instead of concentration. Accordingly  $q'$  is different from  $q$ , and expresses the heat absorbed when 18 kilograms of water vapour are given off from the hydrate

at  $P$  and  $T$ , disregarding the fact that a part of the heat is spent in doing the work  $PV$  which accompanies the expansion of the evaporating kilogram-molecule of water;  $q$  in the first equation, on the contrary, is the 'pure' heat of reaction, so that the relation

$$q = q' - APV = q' - 2T$$

subsists, or

$$\frac{q' - q}{2T^2} = \frac{1}{T}.$$

That, however, represents the difference between

$$\frac{d \log P}{dT} \text{ and } \frac{d \log C}{dT},$$

since

$$APV = 2T,$$

and therefore

$$AP = 2CT,$$

so that

$$\log P - \log C = \log T + \log \left( \frac{2}{A} \right),$$

or

$$\frac{d \log P}{dT} - \frac{d \log C}{dT} = \frac{1}{T}.$$

The proof of the equation for  $P$  given on p. 59 is therefore also a proof of the present equation for  $C$ .

(b) *Non-electrolytes.* The fundamental equations

$$\Sigma n \log C = k \text{ and } \frac{dk}{dT} = \frac{q}{2T^2}$$

may be applied to solid or liquid bodies of slight solubility, and then take the simple form:

$$\frac{d \log C}{dT} = \frac{q}{2T^2},$$

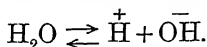
a test of which was given on p. 37.

(c) *Half-electrolytes.* *Influence of temperature on the dissociation of water*<sup>1</sup>. As the quantitative determination of the dissociation of water and the agreement found between different methods (p. 131) is of fundamental importance for the theory of solutions, so too a brilliant

<sup>1</sup> Kohlrausch and Heydwiller, *Sitz.-Ber. der K. Preuss. Akad. d. Wiss.*, March, 1894; *Zeitschr. f. Phys. Chem.* 14. 317.

confirmation is obtained in the agreement between the above equations as applied to the influence of temperature on the electrolytic dissociation of water and the results of experiment.

Here we are concerned with the equilibrium



Application of the fundamental equations

$$\Sigma n \log C = k \text{ and } \frac{dk}{dT} = \frac{q}{2T^2}$$

involves the following quantities and the equilibrium conditions between them :

1.  $C_{\text{H}} = C_{\text{OH}}$  concentration of the electrolytically dissociated liquid water.
2.  $c$  concentration of water vapour.
3.  $c_{\text{H}} = c_{\text{OH}}$  concentration of the electrolytically dissociated water vapour.

These equations are then obtained :

(a) Homogeneous equilibrium in vapour between water and its ions :

$$\frac{d}{dT} (2 \log c_{\text{H}} - \log c) = \frac{q_1}{2T^2}.$$

(b) Heterogeneous equilibrium between the ions in liquid and vapour :

$$\frac{d}{dT} (2 \log C_{\text{H}} - 2 \log c_{\text{H}}) = \frac{q_2}{2T^2}.$$

(c) Change of concentration of steam with temperature :

$$\frac{d \log c}{dT} = \frac{q_3}{2T^2}.$$

Summation of these gives

$$\frac{2 d \log C_{\text{H}}}{dT} = \frac{q_1 + q_2 + q_3}{2T^2},$$

in which

$q_1$	is the heat developed in the change	$\text{H}^+$ vapour + $\text{OH}^-$ vapour = $\text{H}_2\text{O}$ vapour
$q_2$	„ „	$\text{H}^+ + \text{OH}^- = \text{H}^+$ vapour + $\text{OH}^-$ vapour
$q_3$	„ „	$\text{H}_2\text{O}$ vapour = $\text{H}_2\text{O}$

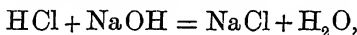
so that

$$q_1 + q_2 + q_3 = q \text{ developed in the change } \overset{+}{\text{H}} + \overset{-}{\text{OH}} = \text{H}_2\text{O};$$

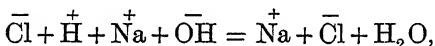
hence  $q$  is the heat developed on formation of water from its ions. The fundamental equation becomes, therefore,

$$\frac{d \log C_{\text{H}}}{dT} = \frac{q}{4T^2}.$$

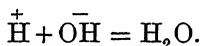
This quantity of heat  $q$  is given calorimetrically in a very simple manner as the heat of neutralization of a completely dissociated (i. e. a strong) acid and base; in the case, e. g., of



or



or



This quantity, according to Thomsen, is 14247 at 10.14°, and 13627 at 24.6°.

According to the latest determinations, the degree of dissociation, i. e.  $C_{\text{H}}$  in gram-ions per litre, is:

0°	2°	10°	18°	26°	34°	42°	50°
0.35	0.39	0.56	0.8	1.09	1.47	1.93	$2.48 \times 10^{-7}$

So, for instance, at 26°  $1.09 \times 10^{-7} \times 18$  grams of water per litre are in the dissociated condition.

Taking  $q$  as constant for a first approximation, and using the integrated form

$$\log \frac{C'_{\text{H}}}{C''_{\text{H}}} = \frac{q}{4} \left( \frac{1}{T''} - \frac{1}{T'} \right),$$

then

$q$	from observations between	0° and 50°	$q_{25} = 13810$
$q$	"	2° " 42°	$q_{22} = 13850$
$q$	"	10° " 34°	$q_{22} = 13970$
$q$	"	18° " 26°	$q_{22} = 13460$

There is thus a very good agreement between values of  $q$  obtained calorimetrically and the measurements of dissociation.

(d) *Electrolytes. Influence of temperature on the solu-*



bility of slightly soluble salts<sup>1</sup>. In the case of electrolytes, whose law of dissociation is unknown, the equation of p. 153,

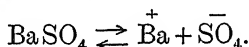
$$\Sigma n i \log C = k,$$

can only be used in combination with

$$\frac{dk}{dT} = \frac{q}{2T^2}$$

if one ignores the variation of  $i$ , i.e. of the electrolytic dissociation with the temperature. That, however, is only permissible in the limiting case of extreme dilution, when the dissociation into ions may be regarded as complete.

An elegant confirmation of this conclusion is to be found in the change of solubility of slightly soluble electrolytes with temperature. For barium sulphate, e. g., the equilibrium between soluble and insoluble salt is expressible by



The equation of equilibrium

$$\Sigma n i \log C = k$$

then becomes

$$i \log C = k,$$

in which  $i$  is the number of ions, and accordingly we get

$$\frac{d \log C}{dT} = \frac{q}{2iT^2}.$$

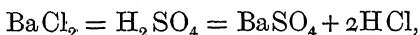
The concentration at different temperatures may be found by measuring the conductivity of the saturated solution, and comparing with the molecular conductivity.

The following results have been obtained for  $V = \frac{1}{C}$ , the volume in litres per gram-molecule :

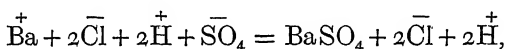
Salt.	Temp.	$V$	$q$ (calc.)	$q$ (obs.)
BaSO <sub>4</sub> . . .	18.4°	50055		
„ . . .	37.7°	37282	5500	5583
AgCl . . .	13.8°	102710		
„ . . .	26.5°	55120	15992	15850

<sup>1</sup> Hollemann, *Zeitschr. f. Phys. Chem.* 12. 125 ; Kohlrausch, *Rose*, l. c. 234 ; Goodwin, l. c. 13. 645.

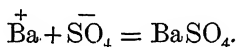
The value found calorimetrically—in other words, the heat evolved when a kilogram-molecule of  $\text{BaSO}_4$  is precipitated from solution in water—is measured as the heat of formation of  $\text{BaSO}_4$  from any pair of sufficiently dissociated salts; i. e. the following change takes place:



which, on account of the electrolytic dissociation of the dissolved salts, comes to



or simply



### C. General Conclusions. Connexion with the Rules already developed, and Extension of them.

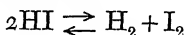
Hitherto in dealing with the phenomena of equilibrium our chief object has been to apply the results of the fundamental equations quantitatively to as many special cases as possible. It remains to draw from those equations certain conclusions which, it is true, are not only qualitative, but are important on account of their perfectly general nature. Secondly, these general rules of equilibrium, which apply essentially only to dilute solutions and gases, will be applied to the phenomena of equilibrium previously studied without that restriction.

#### 1. General Conclusions.

(a) *Influence of change of volume and pressure on chemical equilibrium.* A conclusion from the fundamental equation

$$\sum n \log C = k$$

for equilibrium in gases, which has already been considered in a special case—that of hydriodic acid—may be put in very simple form. According to the equation



we have

$$\log C_{\text{I}_2} + \log C_{\text{H}_2} - 2 \log C_{\text{HI}} = k.$$

If, to start with, there be  $a$  molecule  $H_2$  and  $b$  molecule  $I_2$ , in volume  $V$ , and they are converted to the extent  $x$  before equilibrium is reached,

$$\log \frac{a-x}{V} + \log \frac{b-x}{V} - 2 \log \frac{2x}{V} = k,$$

so that  $V$  disappears from the equation, leaving

$$\log \frac{(a-x)(b-x)}{4x^2} = k.$$

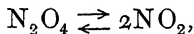
The equilibrium is therefore independent of the volume.

The same is, however, quite generally true when  $\Sigma n_1$  for the first system (in this case  $2HI$ , so that  $\Sigma n_1 = 2$ ) is equal to  $\Sigma n_2$  for the second system (in this case  $H_2 + I_2$ , so that  $\Sigma n_2 = 2$ ). In such cases the two systems consist of the same number of molecules, and therefore, according to Avogadro's law, the volume is not altered by the reaction; thus:

'If displacement of the equilibrium does not involve change of volume, then change of volume has no influence on the equilibrium.'

A second, equally general, relation governs the direction of the displacement of equilibrium, with change of volume for cases in which the latter is of influence.

Making use again of a special case,



we have

$$2 \log C_{NO_2} - \log C_{N_2O_4} = k,$$

or, starting from  $N_2O_4$  with unit quantity in volume  $V$  and conversion of  $x$  for equilibrium,

$$2 \log \frac{x}{V} - \log \frac{1-x}{V} = k,$$

or

$$\log x^2 - \log (1-x) = k + 2 \log V - \log V = k + \log V.$$

Increase of  $V$ , of the volume, leads to increase of  $x$ , of  $NO_2$ .

Applying this to the general case, we get

$$\begin{aligned} \log (A_1 + x)(B_1 + x)(\&c.) - \log (A_2 - x)(B_2 - x)(\&c.) \\ &= k + (\Sigma n_+ - \Sigma n_-) \log V. \end{aligned}$$

where  $A_1, B_1$ , &c., are the quantities of the first system,  $A_2, B_2$ , &c., of the second, originally present; and  $n_1, n_2$ , similarly, the number of molecules. Choosing the first and second systems in such a way that  $\Sigma n_1 > \Sigma n_2$ , an increase of volume will obviously favour the first system, which is that one for which the number of molecules is the greater, and which therefore occupies the greater volume; in other words:

‘Increase of volume favours the system possessing the greater volume.’

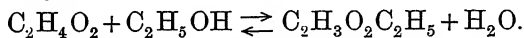
It should be noted that the converse case is implied in this law, and that accordingly the first law, referring to the case of no volume change, is an immediate consequence of it. It is important that the law applies not only to gases, but governs all displacements of equilibrium. The same is true of the alternative form:

‘Increase of pressure favours the system possessing the smaller volume.’

(b) *Influence of change of temperature on chemical equilibrium.* An equally general conclusion as to the influence of change of temperature may be drawn from the equations

$$\Sigma n \log C = k \quad \text{and} \quad \frac{dk}{dT} = \frac{q}{2T^2}.$$

Consider again the case of esterification already dealt with, and symbolized by



It has been remarked (p. 146) that change of temperature is almost without influence on the condition of equilibrium in this case, in accordance with the small value of  $q$ . We

may now add that, generally, when  $q = 0$  also  $\frac{dk}{dT} = 0$ ,

and therefore no displacement of equilibrium is produced by change of temperature if the displacement is not accompanied by a heat change. This case is strictly realized in the equilibrium between optical isomers, such as laevo-

and dextro-amyl alcohol. The heat of conversion  $q$  is here strictly zero at all temperatures, since the two forms have internal structures which are the reflected image of one another; so the inactive mixture, which is in equilibrium at a definite temperature, remains inactive at all temperatures.

It results then that change of temperature has no influence on equilibria which on displacement produce no evolution of heat, and therefore no change of temperature. If there is evolution of heat, temperature has an influence, and in which direction is shown by the following argument.

Remembering that in

$$\frac{dk}{dT} = \frac{q}{2T^2},$$

$q$  is the heat evolved on formation of the first system, whilst in

$$\Sigma n \log C = k$$

the first system appears with negative sign, it follows at once that

$$q = + \text{ corresponds to } \frac{dk}{dT} = + \quad (1)$$

or the second system grows at the expense of the first on rise of temperature;

$$q = - \text{ corresponds to } \frac{dk}{dT} = - \quad (2)$$

or the first system grows at the expense of the second on rise of temperature.

Both rules may be brought under one expression:

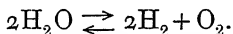
'Rise of temperature favours the system formed with absorption of heat.'

The great value of this law, again, is that it covers all the phenomena of equilibrium, both chemical and physical; e.g. evaporation, in which the vapour formed with absorption of heat increases in quantity with rise of temperature.

It follows from this law that all equilibria are displaced at high temperatures towards the side that is formed with

absorption of heat; whilst at low temperatures a displacement in the opposite sense takes place. When we remember that the temperature of our surroundings is comparatively low, only about  $273^{\circ}$  removed from the absolute zero, it is clear that under the conditions usually obtaining the majority of chemical equilibria tend to the side of the system formed with evolution of heat.

This prediction is verified in the clearest manner in all parts of chemistry; it is however necessary to go more closely into the data, for in many cases the true character of the equilibrium is disguised. Consider more exactly the equilibrium



It is well known that Deville discovered this, by observing the partial decomposition of water at  $1000^{\circ}$ .

On cooling this equilibrium must be displaced, in accordance with the above principle, towards the side formed with evolution of heat, i.e. water, and this has been experimentally verified. The displacement implies that at ordinary temperatures water is the stable form of a mixture of oxygen and hydrogen; the latter accordingly is, under the most varied circumstances, completely transformed into water.

Since now, at ordinary temperatures, chemical equilibrium in general tends to the side of that system which is formed with evolution of heat, it may be foreseen that such chemical changes as take place completely at ordinary temperatures are for the most part accompanied by evolution of heat.

Analogous considerations lead to the conclusion that the reverse must be true at high temperatures. Both conclusions are most completely verified by experience. Indeed a law was stated by Thomsen, and especially by Berthelot—by the latter under the name of the ‘principle of maximum work’—that all chemical reactions which take place of their own accord are accompanied by evolution of heat.

According to what precedes, that would mostly be true under ordinary circumstances, i. e. for the temperature of our surroundings. It would only be strictly true at the absolute zero, as the equation

$$\frac{dk}{dT} = \frac{q}{2T^2}$$

shows. Integrated it gives

$$k = -\frac{q}{T} + \text{const.},$$

so that for  $T = 0$ ,  $k = -\infty q$ .

In conjunction with  $\Sigma n \log C = k$  it follows that

$$\Sigma n_2 \log C_2 - \Sigma n_1 \log C_1 = -\infty q,$$

and therefore either  $C_1$  or  $C_2 = 0$  according as  $q$  is negative or positive, i. e. either the first or the second system disappears completely, according as the first is formed with absorption or evolution of heat. This again may be put into one expression:

‘At the absolute zero point, compounds formed with evolution of heat replace the others completely.’

## 2. *Connexion with the Rules already developed.*

There remains one problem, that of applying the conditions of equilibrium just found to the phenomena of equilibrium treated in the first section especially in the more complex cases last dealt with, that three or four substances take part in the equilibrium. Since the treatment for the case of three substances is contained in the lectures on the formation and dissociation of double salts, which have been published separately<sup>1</sup>, we will here discuss only the case of chemical equilibrium between four substances, in connexion with the former example of two salts which suffer double decomposition. We may then generalize the results of the particular case in Löwenherz's

<sup>1</sup> *Bildung und Spaltung von Doppelsalzen*. Engelmann, Leipzig, 1896.

research<sup>1</sup>, at least so far as we have to deal with easily soluble salts, and the laws of dilute solutions are applicable.

Let us take any pair of salts without a common ion which follow the law of dissociation (p. 130), and whose saturated solutions are so dilute that practically complete dissociation may be assumed. Expressing them by the formulae  $\text{KCl}$  and  $\text{NaNO}_3$  in order to avoid abstractions as much as possible, then the potential existence of  $\text{NaCl}$  and  $\text{KNO}_3$  is given. Let us now glance at all the possibilities that arise in consequence of the contact of such salts with water, on the assumption that no isomorphism or formation of double salts introduces further complications.

We have first the four solutions saturated with single salts, whose concentrations are given by

$$C_{\text{KCl}}, C_{\text{NaNO}_3}, C_{\text{KNO}_3}, \text{ and } C_{\text{NaCl}}.$$

Secondly, we have to consider the pairs of salts with a common ion, say  $\text{KCl}$  and  $\text{NaCl}$ . The possibilities in this

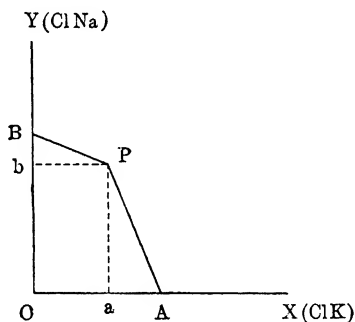


FIG. 50.

case may be shown graphically by the mass of  $\text{KCl}$  and of  $\text{NaCl}$  in a given mass of water, represented along two axes  $ox$  and  $oy$  (Fig. 50). The concentration of the saturated

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 13. 459.



solution of KCl alone,  $C_{\text{KCl}}$ , is then figured along OX as OA;  $C_{\text{NaCl}}$  along OY as OB. From A a curve proceeds which represents saturation with KCl on gradually increasing content of NaCl. Assuming Ostwald's law of dissociation, and remembering that the concentration of the undissociated potassium chloride, on account of saturation, is constant, we have

$$C_{\text{K}} C_{\text{Cl}} = \text{const.},$$

or the product of the concentration of the potassium and chlorine ions is constant; the constant in question is given by means of the concentration of the solution saturated with KCl alone, as  $C_{\text{KCl}} = \text{OA}^2$ , since almost complete dissociation is assumed and the concentration of the salt is therefore the same as that of the ions.

In the same way a curve starts from B, representing saturation with NaCl on increasing content of KCl.

The two curves meet at a point P which corresponds to saturation with both NaCl and KCl, and whose co-ordinates  $Pa$  and  $Pb$  satisfy the two equations

$$Pa(Pa + Pb) = \text{OB}^2 \quad \text{and} \quad Pb(Pa + Pb) = \text{OA}^2,$$

whence we get

$$(Pa + Pb)^2 = \text{OB}^2 + \text{OA}^2.$$

P is therefore given by a simple construction: joining B and A we have (Fig. 51)

$$\text{AB} = Pa + Pb.$$

A perpendicular OC on AB divides AB into parts equal to  $Pa$  and  $Pb$ , since

$$\text{CB} : \text{BO} = \text{BO} : \text{BA},$$

so that

$$\text{CB} = \frac{\text{OB}^2}{\text{BA}} = \frac{\text{OB}^2}{Pa + Pb} = Pa.$$

In the third place we are concerned with the possibility of three salts, and it is best to arrange, after Löwenherz,

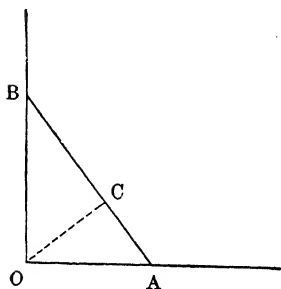
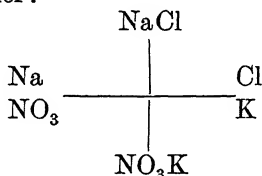


FIG. 51.

the four combinations of two salts with a common ion in the following order:—



and to represent each combination in one plane by pairs of axes which do not, as previously, make an angle of  $90^\circ$ , but of  $60^\circ$  with one another. In this way the axes along which  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{KNO}_3$ ,  $\text{NaNO}_3$  are measured form the edges of an octahedron on whose faces the combination of two salts is shown.

It may be added that this graphical representation may be reduced to the more easily intelligible form of rectangular

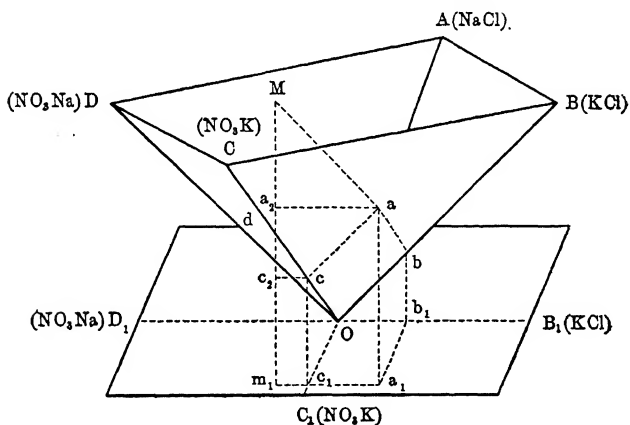
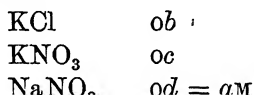


FIG. 52.

co-ordinates. If we have, e.g., a solution in which for 1000 molecules of water the following quantities (in molecules or equivalents) of salt are contained, as represented by the lines in Fig. 52,



the composition in question is represented by the point *m*, since

$$ca // ob \quad ab // oc \quad am // od.$$

The same position may be reached with the aid of two axes, *OB*<sub>1</sub>, *OC*<sub>1</sub>, in the horizontal plane and a third vertically through *o*. We have then:

$$\text{KCl} \quad \text{on } OB_1 \text{ as } ob_1 = \frac{1}{2} ob \sqrt{2},$$

$$\text{KNO}_3 \quad ,, \quad OC_1 \quad ,, \quad oc_1 = b_1 a_1 = \frac{1}{2} oc \sqrt{2},$$

$$\text{NaNO}_3 // OD_1 \quad ,, \quad a_1 m_1 = \frac{1}{2} am \sqrt{2} = \frac{1}{2} od \sqrt{2}$$

and vertically

$$m_1 M = Ma_2 + a_2 c_2 + c_2 m_1,$$

in which

$$Ma_2 = \frac{1}{2} Ma \sqrt{2} = \frac{1}{2} od \sqrt{2}; \quad a_2 c_2 = \frac{1}{2} ac \sqrt{2} = \frac{1}{2} ob \sqrt{2}$$

$$c_2 m_1 = cc_1 = \frac{1}{2} oc \sqrt{2},$$

so that

$$m_1 M = \frac{1}{2} (od + ob + oc) \sqrt{2}.$$

Choosing a suitable unit, so as to multiply all the previous lengths by  $\frac{1}{2}\sqrt{2}$ , Löwenherz's mode of representation may thus be reduced to a rectangular co-ordinate system, the quantities of the single salts, in gram-molecules (or equivalents), being represented on the horizontal axes, and on the vertical axis the sum of these quantities.

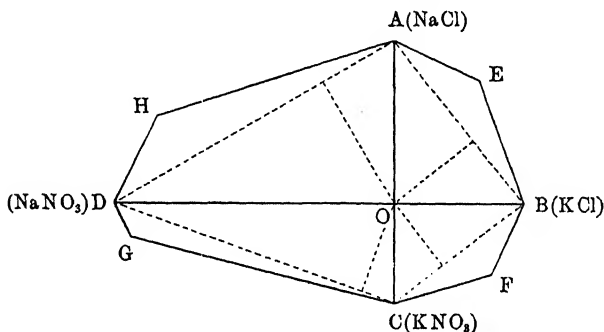


FIG. 53.

As an example let us take the data for the salts KCl, NaCl, KNO<sub>3</sub>, and NaNO<sub>3</sub> at 25°:

NaCl	100H <sub>2</sub> O	11.1 NaCl	$C_{\text{NaCl}} = 11.1$
KCl	"	8.7 KCl	$C_{\text{KCl}} = 8.7$
KNO <sub>3</sub>	"	6.8 KNO <sub>3</sub>	$C_{\text{KNO}_3} = 6.8$
NaNO <sub>3</sub>	"	19.3 NaNO <sub>3</sub>	$C_{\text{NaNO}_3} = 19.3$

The values in question have next to be measured along the axes OA, OB, OC, OD in the horizontal plane. Saturation with a combination of two salts with a common ion leads by the construction p. 161 to the following points (Fig. 53):—

NaCl, KCl . . . . .	E
KCl, KNO <sub>3</sub> . . . . .	F
KNO <sub>3</sub> , NaNO <sub>3</sub> . . . . .	G
NaNO <sub>3</sub> , NaCl . . . . .	H

We have finally to consider solutions saturated with three salts, and may set as possible combinations

NaCl, KCl, KNO <sub>3</sub> . . .	(1)	NaCl, KCl, NaNO <sub>3</sub> . . .	(3)
NaCl, KNO <sub>3</sub> , NaNO <sub>3</sub> . . .	(2)	KCl, KNO <sub>3</sub> , NaNO <sub>3</sub> . . .	(4)

The simultaneous existence of KNO<sub>3</sub> and NaCl in (1) or (2) on the one hand and the reciprocal system NaNO<sub>3</sub> and KCl in (3) or (4) on the other, is only possible at one definite temperature, since if the four salts KCl, NaCl, KNO<sub>3</sub>, and NaNO<sub>3</sub> could exist in stable form side by side, they could do so in contact with any solution that is saturated with them all. Therefore we have the conditions :

Saturation with KNO <sub>3</sub> . . . . .	$C_{\text{K}} C_{\text{NO}_3} = C_{\text{KNO}_3}^2$
" " NaCl . . . . .	$C_{\text{Na}} C_{\text{Cl}} = C_{\text{NaCl}}^2$
" " NaNO <sub>3</sub> . . . . .	$C_{\text{Na}} C_{\text{NO}_3} = C_{\text{NaNO}_3}^2$
" " KCl . . . . .	$C_{\text{K}} C_{\text{Cl}} = C_{\text{KCl}}^2$

from which it follows that the two reciprocal systems of salts are only possible at a temperature for which

$$C_{\text{KNO}_3} C_{\text{NaCl}} = C_{\text{NaNO}_3} C_{\text{KCl}}.$$

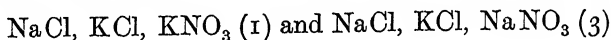
But by the above

$$C_{\text{KNO}_3} C_{\text{NaCl}} = 6.8 \times 11.1 = 75.48,$$

whilst

$$C_{\text{NaNO}_3} C_{\text{KCl}} = 19.3 \times 8.7 = 167.91.$$

One of the two systems will therefore be converted into the other, and in fact that with the greater product of concentrations—here  $C_{\text{NaNO}_3}$  and  $C_{\text{KCl}}$ —will be unstable with regard to the other. Comparing, e. g., the two solutions



which are saturated with the reciprocal couples in question,  $\text{NaCl, KNO}_3$  and  $\text{KCl, NaNO}_3$ , and in addition with  $\text{KCl}$  and  $\text{NaCl}$  respectively, we have

$$(3) \quad C_{\text{Na}} C_{\text{Cl}} = C_{\text{NaCl}}^2 \quad C_{\text{K}} C_{\text{Cl}} = C_{\text{KCl}}^2 \quad C_{\text{Na}} C_{\text{NO}_3} = C_{\text{NaNO}_3}^2,$$

so that

$$C_{\text{NO}_3} \cdot C_{\text{K}} = \frac{C_{\text{KCl}}^2 C_{\text{NaNO}_3}^2}{C_{\text{NaCl}}^2},$$

but in (1)

$$C'_{\text{NO}_3} \cdot C'_{\text{K}} = \frac{C_{\text{KNO}_3}^2 C_{\text{NaCl}}^2}{C_{\text{NaCl}}^2},$$

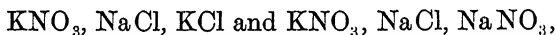
so since

$$C_{\text{KCl}} C_{\text{NaNO}_3} > C_{\text{KNO}_3} C_{\text{NaCl}},$$

it follows that

$$C_{\text{NO}_3} \cdot C_{\text{K}} > C_{\text{NO}_3} \cdot C'_{\text{K}}.$$

Accordingly the solution (3) saturated with  $\text{NaCl, KCl}$ , and  $\text{NaNO}_3$  would be supersaturated with  $\text{KNO}_3$ . We have then to consider, and to represent graphically, only the cases



whose four ionic concentrations, e. g. in the second case, are fixed by the conditions

$$C_{\text{K}} C_{\text{NO}_3} = C_{\text{KNO}_3}^2 \quad C_{\text{Na}} C_{\text{Cl}} = C_{\text{NaCl}}^2 \quad C_{\text{Na}} C_{\text{NO}_3} = C_{\text{NaNO}_3}^2,$$

and

$$C_{\text{K}} + C_{\text{Na}} = C_{\text{Cl}} + C_{\text{NO}_3}.$$

The problem may be solved numerically and graphically in the following way:—

We have

$$(C_{\text{Na}} + C_{\text{K}}) C_{\text{Na}} = (C_{\text{NO}_3} + C_{\text{Cl}}) C_{\text{Na}} = C_{\text{NaNO}_3}^2 + C_{\text{NaCl}}^2$$

$$\text{and} \quad 1 + \frac{C_{\text{K}}}{C_{\text{Na}}} = 1 + \frac{C_{\text{K}} C_{\text{NO}_3}}{C_{\text{Na}} C_{\text{NO}_3}} = 1 + \frac{C_{\text{KNO}_3}^2}{C_{\text{NaNO}_3}^2},$$

therefore

$$(C_{\text{Na}} + C_{\text{K}})^2 = \frac{(C_{\text{NaNO}_3}^2 + C_{\text{NaCl}}^2)(C_{\text{NaNO}_3}^2 + C_{\text{KNO}_3}^2)}{C_{\text{NaNO}_3}^2},$$

so that in Fig. 54

$$(C_{\text{Na}} + C_{\text{K}})^2 = \frac{AD^2 \cdot CD^2}{OD^2}$$

or

$$(C_{\text{Na}} + C_{\text{K}}) : AD = CD : OD,$$

whence

$$C_{\text{Na}} + C_{\text{K}} \text{ is given as } DC' \text{ by making } DO' = AD.$$

Therefore also

$$C_{\text{Cl}} + C_{\text{NO}_3} = DC'.$$

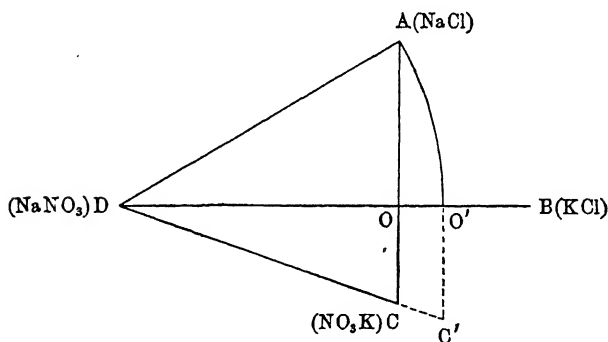


FIG. 54.

To calculate and represent the separate ionic concentrations we have then :

$$C_{\text{Na}} : C_{\text{K}} = C_{\text{NO}_3} C_{\text{Na}} : C_{\text{NO}_3} C_{\text{K}} = C_{\text{NaNO}_3}^2 : C_{\text{NO}_3\text{K}}^2 = OD^2 : OC^2$$

$$C_{\text{NO}_3} : C_{\text{Cl}} = C_{\text{NO}_3} C_{\text{Na}} : C_{\text{Cl}} C_{\text{Na}} = C_{\text{NaNO}_3}^2 : C_{\text{NaCl}}^2 = OD^2 : OA^2.$$

The first relation leads to  $C_{\text{Na}}$  and  $C_{\text{K}}$  by taking  $DC'$  (Fig. 55) =  $C_{\text{Na}} + C_{\text{K}}$ ; then  $C_{\text{NaNO}_3} = OD$  (Fig. 54) is measured from  $c'$  vertically as  $c'd_1$ ; at right angles to it  $d_1a = C_{\text{NaCl}} = OA$  (Fig. 54); then from  $d_1$  the perpendicular  $d_1g$  on to  $ac'$ , and finally  $ge \parallel ad$ . We have then :

$$ga : ad = ad_1 : ac' \text{ and } ac' : c'd_1 = c'd_1 : c'a.$$

therefore

$$eD : ec' = ag : gc' = ad_1^2 : c'd_1^2 = C_{\text{NaCl}}^2 : C_{\text{NaNO}_3}^2,$$

and accordingly

$$eD = C_{\text{Cl}} \text{ and } ec' = C_{\text{NO}_3}.$$

In the same way  $C_{\text{Na}}$  and  $C_{\text{K}}$  are found as  $df$  and  $fc'$ .

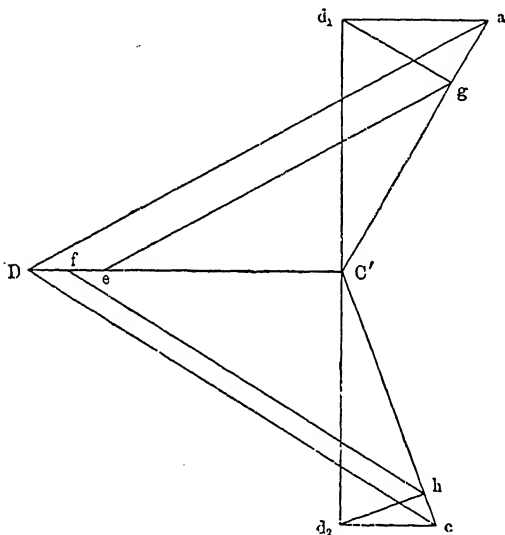


FIG. 55.

The composition of the solution may now be treated as the sum of  $\text{NaNO}_3$  and  $\text{KCl}$ , together with

$\text{KNO}_3$  if  $\text{NO}_3 > \text{Na}$ ,

or  $\text{NaCl}$  if  $\text{NO}_3 < \text{Na}$ .

The latter is the case, so that

$$\begin{array}{ccc} \text{KCl} & \text{KNO}_3 & \text{NaCl} \\ C_{\text{K}} - C_{\text{NO}_3} & C_{\text{NO}_3} & C_{\text{Na}}. \end{array}$$

For these reasons the point  $\kappa$  is drawn on Fig. 56 representing saturation with  $\text{KNO}_3$ ,  $\text{NaCl}$ , and  $\text{NaNO}_3$ ; and similarly  $\text{L}$  for saturation with  $\text{KNO}_3$ ,  $\text{NaCl}$ , and  $\text{KCl}$ .

Further, in the lower half of Fig. 56, which is a projection on the horizontal plane, certain solubility curves must be drawn, which, for simplicity, we will represent as straight.

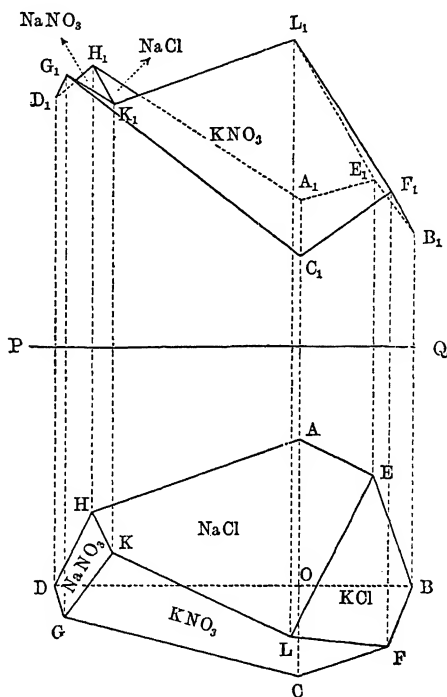


FIG. 56.

Taking first the boundary of the figure in question, the meaning is as follows:—

A, saturation with NaCl alone;

AE       "       "       "       with increasing KCl content;

E       "       "       "       and KCl;

EB       "       "       KCl   with decreasing NaCl content;

B       "       "       "       alone;

BF       "       "       "       with increasing KNO<sub>3</sub> content;

F       "       "       "       and KNO<sub>3</sub>;

FC       "       "       KNO<sub>3</sub> with decreasing KCl content;



C,	saturation with $\text{KNO}_3$ alone;
CG	„ „ „ with increasing $\text{NaNO}_3$ content;
G	„ „ „ and $\text{NaNO}_3$ ;
GD	„ „ $\text{NaNO}_3$ with decreasing $\text{KNO}_3$ content;
D	„ „ „ alone;
DH	„ „ „ with increasing $\text{NaCl}$ content.
H	„ „ „ and $\text{NaCl}$ ;
HA	„ „ $\text{NaCl}$ with decreasing $\text{NaNO}_3$ content.

Then K (saturation with  $\text{NaCl}$ ,  $\text{KNO}_3$ , and  $\text{NaNO}_3$ )  
and L ( „ „  $\text{KCl}$ ,  $\text{KNO}_3$ , and  $\text{KCl}$ )

are to be joined by a line KL which represents saturation with  $\text{NaCl}$  and  $\text{KNO}_3$ . Finally we have to join

H, saturation with  $\text{NaNO}_3$  and  $\text{NaCl}$  alone, by a line corresponding to increasing content of  $\text{KNO}_3$ , to K, where saturation with  $\text{KNO}_3$  occurs;

E, saturation with  $\text{NaCl}$  and  $\text{KCl}$  alone, by a line corresponding to increasing content of  $\text{KNO}_3$ , to L, where saturation with  $\text{KNO}_3$  occurs;

F, saturation with  $\text{KCl}$  and  $\text{KNO}_3$  alone, by a line corresponding to increasing content of  $\text{NaCl}$ , to L, where saturation with  $\text{NaCl}$  occurs;

G, saturation with  $\text{KNO}_3$  and  $\text{NaNO}_3$  alone, by a line corresponding to increasing content of  $\text{NaCl}$ , to K, where saturation with  $\text{NaCl}$  occurs.

These bounding and separating lines divide the whole field into four parts, which correspond each to saturation with one salt; the separating lines correspond to saturation with two salts, and where two of them meet we have saturation with three salts.

The vertical projection given in the upper half of Fig. 56 is constructed according to the principle explained on p. 167, the sum of the number of molecules being measured along the vertical axis.

## II. VELOCITY OF REACTION

COMPARING the branch of the subject dealing with velocity of reaction, with the previous one on the phenomena of equilibrium, the leading difference is seen to be a new factor—the time. Accordingly the experimental data here have been much less completely worked out, especially as thermo-dynamics gives no direct solution of problems in which time is involved. That science is, so far, applicable only to the final state reached—the state of equilibrium.

In agreement with that, a somewhat different mode of treatment is here adopted for velocity of reaction. Whilst all the phenomena with regard to equilibrium may be connected with laws already proved, or at least shown to be highly probable, here a distinction must be made. On the one hand, those results are to be chosen which can be followed out mathematically in their essential character; but on the other there is an extensive collection of material that has not yet been arranged from any unifying point of view. Of this we have chosen what seems to be important in principle, and, so far as can be judged, not too distant in connexion with what has already been systematically explained. The two following sections will therefore serve as basis of division :—

§ 1. Regularities with regard to velocity of reaction.

§ 2. Empirical results in the study of velocity of reaction.

### § 1. REGULARITIES WITH REGARD TO VELOCITY OF REACTION.

The regularities with regard to velocity of reaction, so far as they are known, may be looked at from two points of view.

First, a connexion with thermo-dynamics exists, since the laws governing velocity must be in harmony with those governing the final state of equilibrium. Secondly, however, certain rules may be put forward on the ground of simple kinetic notions, which have so far received good experimental confirmation. We will therefore take in order:

A. Velocity of reaction and equilibrium.

B. Chemical kinetics.

#### A. Velocity of Reaction and Equilibrium.

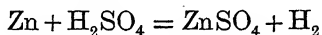
The fact that a reaction needs time for its completion involves that, besides the cause producing it, which we may describe as the 'moving force,' or 'affinity,' a 'resistance' comes into play. The two are therefore to be considered separately, and it may be foreseen that the nature of the resistance can be most varied, whilst the 'moving force' is definite for a given state of matter. The resistance may, e. g., be caused by actual distance between the bodies acting on one another, or by the viscosity of the medium in which the reaction is to take place. The 'moving force,' however, is bound up with the existing state of the body or system of bodies, and the way leading to the final state of equilibrium, and so may be discussed from a general point of view, which must now be done.

#### 1. *Velocity of Reaction and Affinity. Mechanical Measure of Affinity.*

In order to measure the 'moving force' which causes a reaction, it is in general suitable to make use of a measurable opposing force, that may be gradually applied

till it stops the reaction, and on further increase causes a change in the reverse direction. If the change is accompanied by an increase of volume, the opposing force may be an external pressure, and so the 'moving force' or 'affinity' may be measured mechanically.

This method is most obviously applicable to reactions which are accompanied by an evolution of gas, so we will first take one from the researches of Tammann and Nernst<sup>1</sup>, in which the action of zinc on sulphuric acid, with evolution of hydrogen,



is arrested by a measurable pressure. The apparatus consisted of a thick-walled glass tube *ab* (Fig. 57), of about 1 centimetre internal diameter and 20 centimetres length, to which a closed air manometer, formed of a capillary tube, was sealed. The filling was accomplished in the following way:—After the manometer had been filled with dry air and provided with mercury, the zinc was introduced at *b* into the apparatus held upside down, then a quantity of chloroform sufficient to cover it, then a glass rod, and finally the dilute sulphuric acid; since the metal was protected by the chloroform from the attack of the acid, no evolution of hydrogen could take place, and the sealing off at *b* was accomplished with a minimum of waste air-space. When the apparatus was inverted, the heavy chloroform fell to the bottom, while the zinc was held up by the glass rod, over the chloroform, and in the solution; hydrogen was liberated with continuously increasing pressure, which could be read off on the manometer. The accuracy of reading, moreover, was greatly increased by closing the air volume *cd* to be measured by a thread of mercury at each end, whose difference of position could easily be read to 0.1 mm. The length of the

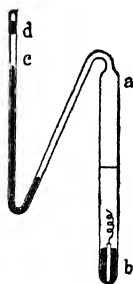


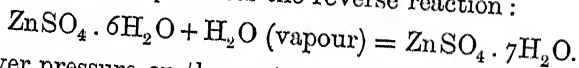
FIG. 57.

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 9. 1.

closed air column was mostly 40 centimetres at atmospheric pressure.

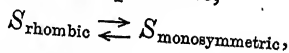
In this way it was found, amongst other cases, that a pressure of 18 atmospheres stops further evolution of hydrogen in 0.13 normal sulphuric acid in contact with zinc, and 1.3 normal in respect of zinc sulphate. And that a higher pressure of hydrogen reversed the reaction, causing precipitation of zinc, was shown by leaving the apparatus to stand at the atmospheric temperature, after it had previously been warmed to increase the pressure.

The circumstances are similar, but simpler, with a hydrated salt. Frowein, e.g. (p. 57), found that zinc sulphate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ) at  $18^\circ$  has a maximum pressure of 8.406 mm., in accordance with the fact that a higher external pressure produces the reverse reaction:



A lower pressure, on the contrary, allows the decomposition to proceed further.

In the previous case we found a pressure that finally stops and reverses the reaction, but it is not the mere mechanical pressure that is effective. An equal pressure of air—say 18 atmospheres—would not, in the case discussed, stop the action of zinc on sulphuric acid. What does oppose the reaction, and shows itself as pressure, is a definite concentration of hydrogen, like the definite concentration of water vapour in hydrates. So we must in the third place turn to cases more specially suited to measure affinity, in which a pressure stops and reverses the reaction indifferently, whether it be exerted by hydrogen or by a piston. These are the transformations taking place without evolution of gas in so-called condensed systems, such as that described (p. 26) for sulphur; the latter consists in complete conversion in one direction or the other according to temperature,



and in such a way that above  $95.6^\circ$ , the temperature of

conversion, monosymmetric sulphur is produced. The conversion, as explained on p. 26, may be stopped by the application of a definite pressure, and made to go the opposite way by a still higher pressure; and, what is essential for our purpose, the pressure ( $p$  in kilograms per sq. metre) which keeps the 'moving force' in equilibrium stands in a simple relation to other quantities, according to the equation of p. 26:

$$Avdp = q \frac{dt}{P}.$$

Here  $v$  is the increase of volume (in cub. metres) on conversion of rhombic into monosymmetric sulphur,  $q$  the heat absorbed in the process,  $P$  the absolute temperature of conversion, and the equation states that at a temperature higher by  $dt$  than the temperature of conversion, a pressure of  $dp$  (kilograms per sq. metre) exactly stops the conversion.

The equation, a direct consequence, or rather an expression, of the second law (as discussed on p. 26), has been repeatedly verified. In the first place it corresponds exactly to the law governing change of melting point with pressure, where  $q$  is the latent heat of fusion,  $v$  the increase of volume on fusion. And then Reicher verified the above formula experimentally, while Mallard and Le Chatelier<sup>1</sup> did the same for the conversion of silver iodide, which at 146° passes from hexagonal to regular. Roozeboom<sup>2</sup>, finally, has verified the equation for the fusion of the hydrate  $\text{HBr} \cdot 2\text{H}_2\text{O}$  at  $-11.3^\circ$ , which is due to chemical decomposition.

This equation, based on thermo-dynamic reasoning and verified by experiment, may now be used to answer our question on the moving force in reactions. It determines not only the force or pressure which a transformation can overcome, or that which suffices to stop or reverse the reaction, but also—and the formulation is then simpler—

<sup>1</sup> *Journ. de Phys.* [2] 4. 305.

<sup>2</sup> *Recueil des trav. Chim. des Pays-Bas*, 5. 358.

how much work can be done in the transformation. This at  $dt$  above the temperature of conversion is  $vdp$  kilogram-metres or  $Avdp$  calories. Writing this as  $dE$ , that is

$$dE = Avdp,$$

we get

$$dE = \frac{qdt}{P}.$$

This work  $dE$  has, however, a more general meaning; it is the work that the conversion itself can accomplish if it overcomes the limiting counterpressure, i. e. the pressure that it can just, or can no more, overcome. Under these conditions the conversion takes place 'reversibly,' and so  $dE$  becomes a constant and completely definite quantity which the conversion can, as a maximum, perform at a given temperature, whether the opposing action is a pressure or anything else, and however the reaction may go. For suppose the reaction to take place in some other way, i. e. by first dissolving the sulphur and then allowing it to crystallize out in the higher form, there being in this case also a limiting opposing force which is just overcome, so that the conversion takes place reversibly. If it were possible in this way to gain some other amount of work  $dE \pm \Delta$ , it would be possible to carry out a reversible cyclic process at constant temperature with gain of work  $\pm \Delta$ , since in the one part  $dE \pm \Delta$  would be gained, and in the reverse process only  $dE$  lost. But the second law of thermo-dynamics, according to which the net work accomplished is proportional to  $dt$ , excludes any evolution or expenditure of work in this case; it makes  $\Delta$  unconditionally zero, and therefore  $dE$  constant, which is thus a more exact formulation of the definite 'moving force' already referred to. The play of affinities in a given body or system of bodies can accomplish a fixed amount of work before equilibrium is attained: an amount which can in certain cases be simply expressed, and stands in a simple relation to the moving force, at least in those cases, such as the transformations just mentioned, in which the

phenomenon proceeds unchanged from moment to moment, and consequently the moving force remains constant during the whole process.

In order that the equation may receive a more general meaning, let us first make its contents clearer by means of a graphical construction. Assuming for simplicity that  $q$  does not vary with the temperature, integration of

$$PdE = qdt$$

gives

$$PE = qt + \text{const.},$$

in which, for  $t = 0$ ,  $E = 0$ , so that

$$PE = qt \quad \text{or} \quad E = \frac{qt}{P}.$$

In this  $E$  is the work that can be accomplished at  $t^\circ$  above the conversion temperature.

Drawing then, on two axes  $OE$  and  $ot$  (Fig. 58),  $oq = q$  and  $OP = P$ , the straight line

$qp$  prolonged to  $Pr$  is the expression of the work which formation of monosymmetric sulphur above  $95.6^\circ$  can accomplish. The work is, e.g.,  $tr$  at a temperature  $Pt = t$  above  $95.6^\circ$ . The graphical treatment affords an insight into the results of the equation that is not easily to be obtained by experiment, and

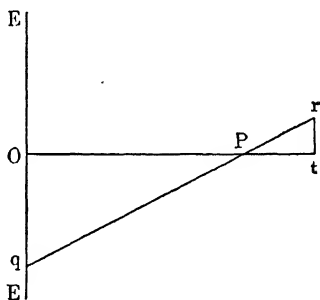


FIG. 58.

that is connected with the change of sign at  $P$ . Below  $P$  the sign of  $E$  is reversed, i. e. the conversion into rhombic sulphur can accomplish work; the amount of the work is given by the straight line  $qp$ , but since contraction occurs the work cannot be made available by means of an external pressure. To obtain it some other mechanism would have to be thought out, but the amount of it is fixed by the above reasoning.

Returning with Fig. 58 to the velocity of reaction, we



come to an easily perceived relation: if the work that the reaction can accomplish is zero, as at  $95.6^\circ$  at P, the velocity is also zero—change of sign in the amount of the work is accompanied by change of sign in the velocity; whereas above  $95.6^\circ$  rhombic sulphur is converted into monosymmetric, below that point the reverse occurs. In short, the reaction goes in the direction of a possible evolution of work<sup>1</sup>. While as to the extent to which the evolution of heat regulates the sense in which the reaction goes, we see that it is only below  $95.6^\circ$  that the reaction evolves heat: above  $95.6^\circ$  the reverse is true.

We have thus at least reached this conclusion as to the velocity of reaction, that the maximum work  $E$  which the reaction can accomplish is a fundamental quantity, and that when it vanishes or changes sign the velocity does the same.

In order to arrive at anything with regard to the magnitude of the velocity, it is necessary to take account of the 'resistance,' which can be done with some success in the domain of electricity.

## 2. *Velocity of Reaction and Affinity. Electrical Measure of Affinity*<sup>2</sup>.

In considering the generation of electricity, which a reaction may cause, we may adhere to the phenomena of conversion just discussed, since lately<sup>3</sup> it has been found possible to measure the work set free electrically. It must first be noted that the electromotive force which a reaction produces corresponds to the 'moving force' in the sense that an equal and opposite electromotive force completely

<sup>1</sup> It has been remarked that the sign of the total work only conditions that of the moving force when the process remains the same from beginning to end.

<sup>2</sup> See Ostwald, 'Das Chemometer,' *Zeitschr. f. Phys. Chem.* 15. 399.

<sup>3</sup> Cohen, l. c. 14. 53; Cohen and Bredig, l. c. 14. 535; Cohen, Bredig and Van't Hoff, l. c. 16. 453; Baur, l. c. 18. 180; Dorn and Völler, *Wied. Ann.* 60. 468.

stops the reaction, for according to Ohm's law the current becomes zero, and therefore according to Faraday the reaction, which accompanies and causes the current, ceases. A greater electromotive force causes the reaction to go in the reverse direction, if only those substances are present at the electrodes which would be produced there by the reaction. Electromotive force, in reactions which generate electricity, is thus completely comparable to pressure in those that are accompanied by increase of volume, and the electromotive force generated by the reaction exactly answers to the limiting counterpressure. Let us follow out the way in which a transformation going reverse ways above and below a fixed temperature may be conducted so as to go hand in hand with production of electric current, and let us choose for the purpose the decomposition and reformation of zinc sulphate ( $\text{Zn SO}_4 \cdot 7\text{H}_2\text{O}$ ), symbolized by



and associated with the temperature limit  $39^\circ$ .

Two glass vessels A and B (Fig. 59), each provided with a pair of electrodes, are to be used; the upper electrode is a piece of metallic zinc, the lower mercury, covered with a layer of mercurous sulphate. The vessel A contains moist  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ; the other, B, contains moist  $\text{Zn SO}_4 \cdot 6\text{H}_2\text{O}$ . Although the two hydrates in the moist state are both stable only at  $39^\circ$ , yet with certain precautions, like those to be attended to in working with supersaturated solutions—especially the closure (with shellac) of the two vessels at the top—it is possible to work with both salts at temperatures other than  $39^\circ$ . To prepare the hexahydrate in B it is then only necessary to warm that vessel

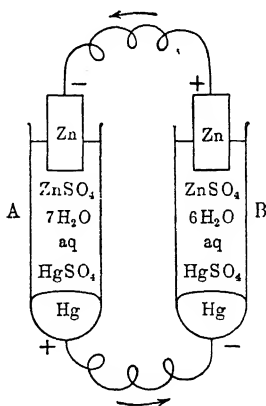
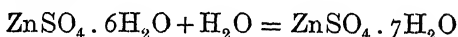


FIG. 59.

above  $39^\circ$  for a sufficiently long time. The whole is then placed in the thermostat and observed in the neighbourhood of  $39^\circ$ . Saturation with  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$  eventually occurs in the two vessels respectively, and may be hastened by the action of a stirrer, not shown in Fig. 59. The behaviour described on p. 63 then shows itself; the solution of the more stable modification is the more dilute, that is, below  $39^\circ$  the  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in A, above  $39^\circ$  the  $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$  in B. At  $39^\circ$  the two solutions are equal. The difference equalizes itself electrically, since the more concentrated solution, say in B below  $39^\circ$ , gives off its salt as ions, the Zn to the zinc rod, the  $\text{SO}_4$  to the mercury, with formation of mercurous sulphate; the zinc in B is therefore positively charged, the mercury negatively. The reverse takes place in A: the zinc gives off positive ions and acquires a negative charge; the mercurous sulphate gives off  $\text{SO}_4$  as negative ions, and therefore positively charged ions of mercury fall into the mass of mercury at the electrode, which acquires a positive charge. The quantities of electricity in question neutralize one another by a current in the sense of the arrows in Fig. 59. But the transformation



is associated with the current, since the removal of zinc sulphate from the solution in B, so long as saturation lasts, results in the dissolving, and therefore disappearance, of  $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ ; while the taking up of zinc sulphate by the solution in A necessarily makes  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  separate out.

If now we measure the electromotive force under which the current accompanying the conversion is produced, and calculate how much work ( $dE$  expressed in calories) is given out in the electrical form, by the conversion of a given mass of zinc sulphate we obtain:

$$dE = \frac{qdt}{P},$$

in which  $q$  is the heat evolved by the conversion of that

amount of zinc sulphate,  $P$  the absolute temperature of conversion, and  $dt$  the remoteness from the conversion-point. Fig. 58 therefore gives a graphical expression of the production of work in the electrical case also, an expression, too, of the experimental results.

The case here considered has the advantage, with regard to velocity of reaction, that not only the 'moving force' or 'affinity' can be calculated and measured as electromotive force, and therefore also the work done  $dE$  can be, but the rate at which the reaction in question takes place can be determined by other data and rules.

The calculable and known electromotive force, shows itself in a current whose intensity is, by Ohm's law,

$$I = \frac{E}{W},$$

where  $W$  is the resistance, external and internal. The external resistance, however, may be made as small as we please, so that  $W$  becomes a quantity depending only on the electrodes, their distance apart, and the properties of the solution, and is therefore measurable by known methods.

According to Faraday's law, a perfectly definite deposition of zinc takes place for a given current running a given time, so that the velocity of reaction is definite too. Thus the nature of the resistance already spoken of (p. 176) which conditions the progress of a chemical reaction is explained, at least in a special case; it depends here on the conductivity of an electrolyte, i. e. on the velocity of movement through the medium in question, under the influence of the moving force, which is here electrical.

### 3. *Velocity of Reaction in Uncondensed Systems.* (*Gases and Dilute Solutions.*)

In the preceding, the simple case was considered of a conversion that is complete, and from beginning to end suffers no variation qualitatively. The moving force is then the same through the whole period of change, and is

closely connected with the work that the conversion is able to perform. In the second place we have to consider reactions which are accompanied by a qualitative as well as a quantitative change—by a change of concentration. The moving force is then different from moment to moment, and may eventually vanish, with the setting in of chemical equilibrium.

As the case previously explained was comparable with fusion and solidification, and the velocity then discussed with the rate of solidification, so here the phenomena may be brought into relation with the physical phenomenon of evaporation, which, in analogy with the change of moving force just referred to, goes more slowly up to the occurrence of equilibrium, here reached when the vapour pressure has risen to a maximum.

In the latter cases the velocity seems to depend on the difference between two functions of the concentration of the two transforming states of aggregation or systems: functions whose equality causes the equilibrium. The velocity is proportional to the difference of velocities, provided there is no other changing factor during the conversion<sup>1</sup>.

The matter is simplest in the act of evaporation: equilibrium occurs when the maximum pressure ( $P$ ) of the evaporating body is equal to the pressure of the vapour ( $p$ ); the rate of evaporation is proportional to the difference between the two quantities, a relation on which the psychrometer of August is based; that is,

Condition of equilibrium . . . . .  $P = p$

Rate of evaporation . . . . .  $k(P - p)$ .

Quite the same relation was found by Noyes and Whitney<sup>2</sup> for the rate of solution of benzoic acid and of lead chloride, since it proved to be proportional to the

<sup>1</sup> Berthelot, *Ann. de Chim. et de Phys.* 65, 66, 68; Guldberg and Waage, *Journ. f. Prakt. Chem.* 19. 83; Planck, *Vorlesungen über Thermodynamik*, 1897, p. 247.

<sup>2</sup> *Zeitschr. f. Phys. Chem.* 23. 689.

difference between the saturating concentration ( $C$ ) and the concentration actually existing ( $c$ ):

Condition of equilibrium . . . . .  $C = c$

Rate of solution . . . . .  $k(C - c)$ .

These relations correspond exactly to those found for chemical reactions which lead to equilibrium.

Starting from the condition of equilibrium found on p. 108,

$$\Sigma n \log C = \text{const.},$$

or

$$\frac{C_2'^{n_2'} C_2''^{n_2''} \dots}{C_1'^{n_1'} C_1''^{n_1''} \dots} = K,$$

in which  $C$  expresses the concentration of the bodies,  $C_1$  of the first,  $C_2$  of the second system;  $n$  the number of molecules of these substances which take part in the reaction. The functions of the concentrations on the two sides whose equality causes equilibrium then give

$$\text{Condition of equilibrium } KC_1'^{n_1'} C_1''^{n_1''} \dots = C_2'^{n_2'} C_2''^{n_2''} \dots$$

and the velocity of reaction is proportional to the difference :

$$\text{Velocity of reaction} = k(KC_1'^{n_1'} C_1''^{n_1''} \dots - C_2'^{n_2'} C_2''^{n_2''} \dots),$$

as appears from the experiments, now to be described, of Meyer and Bodenstein<sup>1</sup> on hydriodic acid, among others. Only it must be remembered that this equation, like the condition of equilibrium with which it is connected, is only correct for sufficient dilution.

The partial decomposition of hydriodic acid, already studied by Hautefeuille<sup>2</sup>, and more thoroughly by Lemoine<sup>3</sup>, has in recent times been the object of an exhaustive investigation by the authors just mentioned. The later researches, which we shall more especially make use of, cover the double problem—the study of the phenomena of equilibrium on the one hand, and that of velocity on the other.

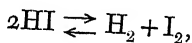
The experiments which refer to equilibrium have already

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 13. 56; 22. 1.

<sup>2</sup> *Compt. Rend.* 64. 608.

<sup>3</sup> *Ann. de Chim. et de Phys.* [5] 12. 145.

been described on p. 108. We need only note from them that the above equation was confirmed. It takes for the equilibrium in question,



the simple form

$$C_{\text{I}_2} C_{\text{H}_2} = K C_{\text{HI}}^2,$$

and at  $440^\circ$  the value of  $K$  was found to be 0.02.

Next we must introduce the rate of decomposition of hydriodic acid. A series of glass bulbs, connected by tubes drawn out in the middle so as to be easily sealed up, was freed from air by means of hydrogen. The gas, before entering the bulbs, was passed through an aqueous solution of hydriodic acid (prepared from its elements); the stream of hydrogen was then stopped, and the solution heated; the gas evolved passed over red phosphorus and phosphorus pentoxide into the bulbs till all the hydrogen was displaced. After being sealed off the bulbs were heated several hours in sulphur vapour (at  $440^\circ$ ), and after an observed interval of time cooled and analyzed. For the velocity, assumed proportional to the difference between the two terms in the preceding equation, we have:

$$-\frac{dC_{\text{HI}}}{dt} = k(KC_{\text{HI}}^2 - C_{\text{H}_2}C_{\text{I}_2}).$$

If the HI originally present is 1 gram-molecule in  $V$  litres, and  $x$  gram-molecules disappear in  $t$  hours, then

$$C_{\text{HI}} = \frac{1-x}{V}, \quad C_{\text{I}_2} = C_{\text{H}_2} = \frac{x}{2V},$$

and accordingly

$$\frac{dx}{dt} = \frac{k}{4V} \{4K(1-x)^2 - x^2\},$$

or

$$\frac{dx}{4K(1-x)^2 - x^2} = \frac{k}{4V} dt,$$

by integration

$$\frac{1}{2a} \log \frac{a(1-x)+x}{a(1-x)-x} = \frac{kt}{4V} + \text{const.},$$

in which

$$a = 2 \sqrt{K} = 2 \sqrt{0.02} = 0.282;$$

and at  $t = 0$   $x = 0$ , so that

$$\text{const.} = 0,$$

and accordingly the expression

$$\frac{1}{t} \log \frac{1 + 2.55x}{1 - 4.55x}$$

must be constant during the reaction, if the volume be unchanged.

The following table contains the results of experiment :

$t$ (hours)	$x$	$\frac{1}{t} \log \frac{1 + 2.55x}{1 - 4.55x}$
5	0.0235	0.0149
15	0.0755	0.0171
60	0.19	0.0173

## B. Chemical Kinetics.

The expression for the velocity of reaction

$$k(C'_2{}^{n'_1} C''_2{}^{n''_2} \dots - KC'_1{}^{n'_1} C''_1{}^{n''_1} \dots),$$

for changes that lead to a final state of equilibrium, may be simplified for the case of reactions that are unlimited, or apparently unlimited. Equilibrium then means the complete predominance of one of the two systems: choosing the one whose concentration is expressed by  $C$ , its prevalence in the final state requires an extremely small value of  $K$ ; the second term in the above expression disappears, and the expression for the velocity becomes

$$kC'^{n'} C''^{n''} \dots$$

Let us then apply this to particular cases, and test it experimentally.

### 1. Monomolecular Reactions. (*Decomposition of Arsine.*)

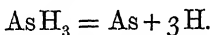
The simplest case included in the above formula is that in which there is only one concentration with whose



changes we are concerned, and in that the value of  $n$  is unity. We then get the mathematical expression

$$-\frac{dC}{dt} = kC.$$

In chemical language this means that a single body is totally or almost totally transformed in the reaction which takes place in a single molecule, as in the decomposition of arsine, according to the equation



The transformation in question is called monomolecular,

and the amount converted in the unit of time is, according to the above expression, proportional to the amount present. That might in any case be expected of such a process.

The apparatus used for the study of the progress of such a reaction has a reservoir A (Fig. 60), into which, after evacuation, the arsine is introduced by the capillary E. E is then sealed off in the blowpipe. The measurement of the quantity present and the quantity decomposed is accomplished by observing the pressure at known volume and temperature. To that end c is filled with mercury,

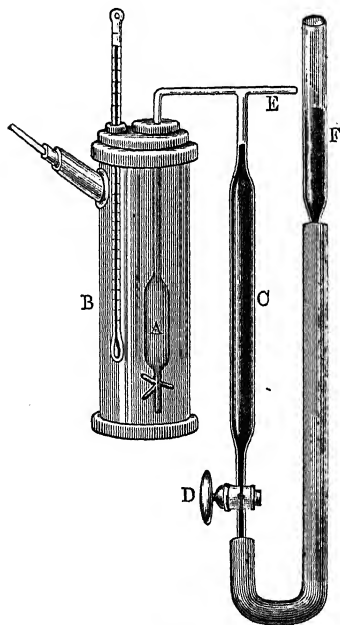


FIG. 60.

and A having been placed with a thermometer in water, the tap D is opened, and by raising or lowering F the mercury is brought to a marked level in c. The difference in level between c and F, together with the barometer reading, gives the pressure of the gas in A at a definite

temperature and volume. The mass of arsine is, however, closely connected with this. Since by decomposition of two molecules of gas, three molecules of hydrogen are produced, besides solid arsenic, the pressure rises during decomposition in the ratio 2:3. If then the original concentration and pressure are  $C_0$  and  $P_0$ , and after  $t$  the pressure has risen to  $P_t$ , then the concentration of the arsine remaining is connected with it in this manner:

$$Pt = P_0 + \frac{1}{2} P_0 \frac{C_0 - C_t}{C_0},$$

so that

$$C_t = C_0 \left( 3 - \frac{2P_t}{P_0} \right).$$

Integrating the fundamental equation we get

$$-\log C_t = kt + \text{const.},$$

and for  $t = 0$

$$-\log C_0 = \text{const.},$$

so that

$$\log \left( \frac{C_0}{C_t} \right) = kt,$$

and accordingly

$$\frac{1}{t} \log \frac{P_0}{3P_0 - 2P_t} = k.$$

The following table contains the results of experiments obtained by heating in diphenylamine vapour ( $310^\circ$ ):—

Time in hours.				Pressure in millimetres.	
$t$				$P$	$k$
0 . . . .				784.84	—
3 . . . .				878.5	0.0908
4 . . . .				904.05	0.0905
5 . . . .				928.02	0.0908
6 . . . .				949.28	0.0905
7 . . . .				969.08	0.0906
8 . . . .				987.19	0.0906

The chemical meaning of the value found for  $k = 0.0906$  appears from the relation

$$-\frac{dC}{Cdt} = k.$$

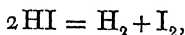
The velocity of decomposition is such that if during an hour the quantity of arsine were maintained constant, by replacing the amount decomposed, then at  $310^{\circ}$  the fraction 0.0906 of that originally present would be decomposed, i. e. 9.06 %. It may be added that the slow progress of such a monomolecular reaction shows that not all the molecules of a gas are in the same condition, else either none would be decomposed or all together. The behaviour recalls Maxwell's assumption that in a gas all temperatures round a certain average occur.

## 2. Bimolecular Reactions.

Proceeding step by step we come to the case that only one concentration changes, but that the change of the body in question is such that two molecules must work together to effect it. The expression for the velocity then becomes

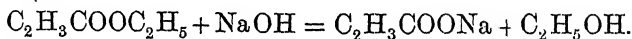
$$-\frac{dC}{dt} = kC^2.$$

Such a case would seem to be the decomposition of hydriodic acid,



and on p. 189 it was shown that the experiments seem to conform to the quadratic expression; but the process of reaction is complicated, because it does not lead to complete decomposition of the hydriodic acid.

We have a second case in which two molecules, but now of different kinds, take part, and which may therefore be called bimolecular, in saponification, e. g., of ethyl acetate by soda:



Since here the two reacting molecules are different, two concentrations,  $C_{\text{I}}$  and  $C_{\text{II}}$ , occur in the fundamental equation. The velocity may be expressed indifferently by  $-\frac{dC_{\text{I}}}{dt}$  or by  $-\frac{dC_{\text{II}}}{dt}$ , since the soda and ethyl acetate dis-

appear molecule for molecule, and therefore at the same rate.

The experiments carried out by Warder<sup>1</sup>, Reicher<sup>2</sup>, Ostwald<sup>3</sup>, and Arrhenius<sup>4</sup> consist in, first, the preparation of, say,  $\frac{1}{20}$  normal potash and  $\frac{1}{20}$  normal ethyl acetate. The flasks containing these liquids are placed (well stoppered) for several hours in a thermostat to acquire a constant temperature. Before the experiment 50 cub. centimetres of each liquid are poured into a previously warmed flask, and the mixture well shaken. For the observation 10 cub. centimetres of this experimental liquid is measured off, and immediately before the time of observation is placed under the burette. Four seconds before the time of observation the tap of the burette is opened and acid allowed to flow in a rapid stream till about 10% less than enough to neutralize. (The requisite quantity can quite well be estimated to 10%.) The flow of acid requires, closely enough, eight seconds. In the following ten to fifteen seconds the acid required to neutralize can be determined with accuracy by careful titration. Or else a known excess quantity of acid may be added and titrated back.

The data may be most conveniently made use of by means of the equation obtained on integrating:

$$-\frac{dC_I}{dt} = kC_IC_{II}.$$

The concentration  $C_I$  is the titre of the alkali at the moment required;  $C_{II}$  is the titre of the ester at the same moment, and is found from the difference between  $C_I$  and the alkali remaining after complete conversion  $C_\infty$ ; if ester is taken in excess, then the excess of it may be measured after the reaction, which makes the determination more convenient; the excess has, obviously, to be added to  $C_I$  to get  $C_{II}$ . Assuming the first case, that of alkali in excess, or

$$C_{II} = C_I - C_\infty \text{ and } -\frac{dC_I}{dt} = kC_I(C_I - C_\infty),$$

<sup>1</sup> *Berl. Ber.* 14. 1361.

<sup>2</sup> *Liebig's Ann.* 228. 257; 238. 276.

<sup>3</sup> *Journ. f. Prakt. Chem.* [2] 35. 112.

<sup>4</sup> *Zeitschr. f. Phys. Chem.* 1. 110.

integration gives

$$\frac{1}{C_{\infty}} \log \frac{C_I}{C_I - C_{\infty}} = kt + \text{const.};$$

and  $C_I = C_0$ , when  $t = 0$ , therefore

$$\text{const.} = \frac{1}{C_{\infty}} \log \frac{C_0}{C_0 - C_{\infty}},$$

and

$$\frac{1}{C_{\infty}} \log \frac{C_I(C_0 - C_{\infty})}{C_0(C_I - C_{\infty})} = kt,$$

whence

$$k = \frac{1}{C_{\infty} t} \log \frac{C_I(C_0 - C_{\infty})}{C_0(C_I - C_{\infty})}.$$

Note that it is not necessary to take as initial concentration that at the moment of mixing; any other moment may be chosen as starting point, and it is well, indeed, not to make the first observation used in the calculations too quickly after mixing. We may reproduce a series from Reicher's experiments at  $9.6^{\circ}$ . Each 100 cub. centimetres of alkali-ester mixture was taken and its titre  $T$  expressed in

$\frac{1}{24.83}$  cub. centimetres of normal liquid. Then

$$\frac{C_I(C_0 - C_{\infty})}{C_0(C_I - C_{\infty})} = \frac{T_I(T_0 - T_{\infty})}{T_0(T_I - T_{\infty})},$$

and

$$C_{\infty} = T_{\infty} \frac{N}{100} = \frac{T_{\infty}}{24.83}.$$

Taking as unit of concentration, as usual, the kilogram-molecule per cub. metre, or the gram-molecule per litre, i. e. normality, we find:

Time in minutes.				Titre of mixture.	
$t$				$T$	$k$
0	.	.	.	61.95	—
4.89	.	.	.	50.59	2.31
11.36	.	.	.	42.40	2.33
29.18	.	.	.	29.35	2.28
$\infty$	.	.	.	14.92	—

The meaning of the constant  $k$  is apparent from the equation

$$k = - \frac{1}{C_I C_{II}} \frac{dC_I}{dt} = 2.3.$$

If  $C_I = C_{II} = 1$ , i. e. if the solution be normal with respect to alkali and ester, and if the transformed materials be continuously replaced, 2.3 times the quantity originally present would be saponified in a minute. The reaction is therefore a very rapid one.

It should be noticed that the equation may be derived from kinetic considerations, since to bring about the change a collision of the two reacting molecules is necessary, and the number of collisions is therefore obviously proportional to the amount of reaction taking place. The number in unit of volume is, however, proportional to both the mass of alkali and of ester,  $C_I$  and  $C_{II}$ , and we get accordingly

$$-\frac{dC_I}{dt} = kC_IC_{II}.$$

The restriction to dilute systems (solutions and gases) which follows from the connexion with the law of equilibrium (p. 187) holds for the kinetic deduction also, since proportionality between the number of collisions and  $C_I$  and  $C_{II}$  is only to be expected in the limiting case when the space taken up by the molecules themselves vanishes by comparison with the total space, which is only true for infinite dilution. Practically the necessary condition holds for tenth-normality and below.

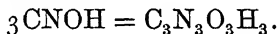
### 3. *Trimolecular Reactions.*

If three molecules are required to complete a reaction, three cases may be distinguished, according as the molecules are all alike, two alike, or all different.

If all are alike the velocity may be taken as proportional to  $C^3$ , in the other cases to  $C^2$ ,  $C_I$  and  $C_I$ ,  $C_{II}$ ,  $C_{III}$  respectively.

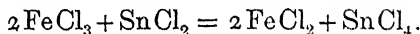
Although, as we shall see later, polymolecular reactions are very rare, an example of each kind may be found.

1. With the molecules all alike, we have formation of cyamelide from cyanic acid :



This we shall have to refer to again.

2. With two molecules alike, the reaction between ferric chloride and stannous chloride <sup>1</sup>,



3. For the case of three different molecules we have the experiments of Noyes and Wason <sup>2</sup> on the reaction between ferrous chloride, potassium chlorate, and hydrochloric acid, studied by Hood <sup>3</sup>. Here we have to do with the equation

$$-\frac{dC_I}{dt} = k C_I C_{II} C_{III}.$$

The determinations were carried out at 20° and the quantity  $x$  of ferrous chloride used up measured by means of permanganate, with the precautions necessary in presence of chlorine. If  $A, B, C$  are the quantities originally present of  $\text{FeCl}_2$ ,  $\text{KClO}_3$ , and  $\text{HCl}$ , expressed in terms of the quantities occurring in the reaction, then after a time  $t$  there remain  $A-x$ ,  $B-x$ , and  $C-x$  respectively, and the equation becomes

$$\frac{dx}{dt} = k(A-x)(B-x)(C-x),$$

from which, by integration,

$$\frac{1}{C-A} \left\{ \frac{1}{A-B} \log \frac{A-x}{B-x} + \frac{1}{C-B} \log \frac{B-x}{C-x} \right\} = kt + \text{const.},$$

and since when  $t = 0$ ,  $x = 0$ :

$$\frac{1}{t(C-A)} \left\{ \frac{1}{A-B} \log \frac{B(A-x)}{A(B-x)} + \frac{1}{C-B} \log \frac{C(B-x)}{B(C-x)} \right\} = k.$$

We will quote a series of observations, and for simplicity of calculation, one in which  $A = B = C$ . The fundamental equation then becomes

$$\frac{dx}{dt} = k(A-x)^3,$$

<sup>1</sup> Noyes, *Zeitschr. f. Phys. Chem.* 16. 546.

<sup>2</sup> Loc. cit. 22. 210.

<sup>3</sup> *Phil. Mag.* [5] 6. 371; 8. 121; 20. 323. See also Schlundt and Warder on the action of  $\text{KI}$ ,  $\text{KClO}_3$ , and  $\text{HCl}$ , *Zeitschr. f. Phys. Chem.* 18. 674; 20. 625.

from which, by integration,

$$\frac{1}{2(A-x)^2} = kt + \text{const.},$$

and since for  $t = 0$ ,  $x = 0$ ,

$$\frac{1}{2A^2} = \text{const.},$$

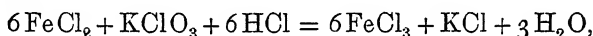
therefore

$$\frac{1}{2(A-x)^2} - \frac{1}{2A^2} = \frac{x(2A-x)}{2A^2(A-x)^2} = kt,$$

or

$$\frac{x(2A-x)}{2A^2(A-x)^2} = k.$$

In the case chosen (at  $20^\circ$ )  $A = B = C = 0.1$ , i. e. in the equation



the hydrochloric acid was decinormal, and the ferrous chloride and potassium chlorate of a strength corresponding to a decinormal value in oxidation and reduction.

<i>Time in minutes.</i>	<i>10 x</i>	<i>10 (A-x)</i>	<i>k</i>
0 . . .	0	1	—
5 . . .	0.048	0.952	1.04
15 . . .	0.122	0.878	0.99
35 . . .	0.238	0.762	1.03
60 . . .	0.329	0.671	1.01
110 . . .	0.452	0.548	1.06
170 . . .	0.525	0.475	1.01

#### 4. *Determination of the Number of Molecules taking part in a Reaction.*

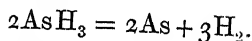
The different forms assumed by the equation according as we are dealing with a transformation of a single molecule, or the mutual action of two or of three, allow conversely of a conclusion as to the number of molecules taking part in the reaction when unknown.

There are essentially two methods. Either one may follow out the course of the reaction in time, when the volume is kept constant, as above, or one may observe the



influence which a change of volume has on the velocity of reaction.

The first method is easily intelligible from what precedes. Suppose the decomposition of arsine to be trimolecular, an assumption that is not excluded by the nature of the process, for it might take place thus:



The equation then, instead of

$$-\frac{dC}{dt} = kC,$$

would be

$$-\frac{dC}{dt} = kC^2,$$

and instead of

$$\frac{1}{t} \log \frac{C_0}{C_t}$$

being constant, we should have

$$\frac{C_I}{t} \left( \frac{1}{C_t} - \frac{1}{C_0} \right)$$

constant: but experiment shows constancy of the former.

Simple as this test is in theory, its indications are often doubtful, for often disturbing influences arise during the reaction, which may entirely distort the view obtained of the reaction.

The other method, based on the varying influence of change of volume on the velocity of reaction, is altogether preferable. Let us set side by side the equations

$$-\frac{dC}{dt} = kC, \quad -\frac{dC}{dt} = kC_I C_{II}, \quad -\frac{dC}{dt} = kC_I C_{II} C_{III}.$$

Passing from the volume  $v$  to that of  $V$  the velocity will, according to the case in question, be changed from

$$\left( \frac{dC}{dt} \right)_v : \left( \frac{dC}{dt} \right)_V = V : v \text{ or } V^2 : v^2 \text{ or } V^3 : v^3$$

respectively, which, if  $v$  and  $V$  differ widely, will cause differences surpassing any anomalies that the reaction may

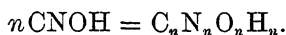
show. The number of molecules  $n$ , i.e. the exponent 1, 2, or 3, may then be directly calculated; for, remembering that the concentration is inversely proportional to the volume, or

$$C_v : C_v = V : v,$$

we get

$$n = \frac{\log \left( \frac{dC}{dt} \right)_v - \log \left( \frac{dC}{dt} \right)_v}{\log C_v - \log C_v}.$$

We will describe such an experiment to determine the number of molecules which take part in the formation of cyanamide from cyanic acid:



The apparatus (Fig. 61) contains cyanic acid in B and is evacuated in A. To obtain this state of things solid cyanuric acid is first placed in C and that tube connected to the air-pump. After evacuation of both A and B the tap between them is closed and C fused off. B is then filled with cyanic acid by heating the cyanuric acid, and finally the mercury in the cylinder is allowed to rise, or the apparatus is lowered until C is cut off from B by mercury. The reaction now proceeds slowly at atmospheric temperature; constant volume is preserved by attending to the level of mercury in the cylinder. The concentration of the cyanic acid present at any moment is calculated from the pressure corresponding to a fixed volume, the mercury in the cylinder being allowed to flow out (by a tap not shown in the figure) till the mercury level below B reaches a mark on the apparatus. When the velocity of reaction has been found, the volume of the gas is doubled by opening the tap between A and B, and the velocity again determined.

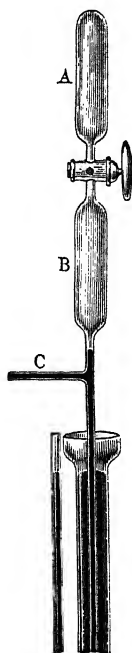


FIG. 61.

Time in hours. $t$	Concentration. $C$	$\frac{\log \left( \frac{dC}{dt} \right)_u - \log \left( \frac{dC}{dt} \right)_v}{\log C_u - \log C_v}$
23 . . .	$\left\{ \begin{array}{l} 188.84 \\ 153.46 \end{array} \right.$	2.9
20 . . .	$\left\{ \begin{array}{l} 79.01 \\ 76.04 \end{array} \right.$	

The reaction is therefore apparently trimolecular. Noyes and Wason (p. 196) have in a similar manner shown the trimolecular character of the action between ferrous chloride, potassium chlorate, and hydrochloric acid.

The method for determination of the number of molecules may be extended in one direction. If in the formula

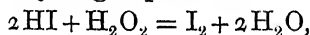
$$-\frac{dC}{dt} = kC_I^{n_I}C_{II}^{n_{II}},$$

one of the concentrations, say  $C_{II}$ , is in any manner made constant (e.g. it may be made very great as compared with the others), then it disappears from the equation, which becomes

$$-\frac{dC}{dt} = k_I C_I^{n_I}, \text{ where } k_I = k C_{II}^{n_{II}}.$$

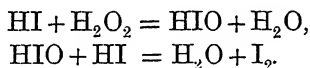
This allows of determining the number of molecules of the component, to which  $C_I$  refers, taking part in the reaction. In this way Ewan<sup>1</sup> showed it to be probable that in the slow oxidation of phosphorus, sulphur, and aldehyde, the oxygen has the coefficient  $\frac{1}{2}$ , pointing to an action of dissociated oxygen (atoms, or ions).

It must be noticed that, so far as the number of molecules has been investigated, it appears that the mechanism of reaction is in general very simple, and nearly always mono- or bi-molecular. If an equation, in order to express a process of reaction quantitatively, shows the interaction of several molecules, it is probably in reality a combination of processes taking place consecutively. The action of hydriodic acid on hydrogen peroxide,

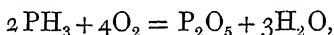


<sup>1</sup> *Zeitschr. f. Phys. Chem.* 16. 321; Van 't Hoff, l. c. 16. 413; Jorissen, l. c. 22. 34, 54; 23. 667.

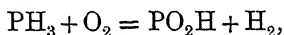
appears to be not tri- but bi-molecular<sup>1</sup>, and apparently takes place by steps, the first process being bimolecular, e. g.



In some cases this opinion in favour of simple processes of reaction occurring by stages is directly confirmed by experiment. This is so with the combustion of phosphoretted hydrogen,  $\text{PH}_3$ , which, taken as a whole, is represented by the equation

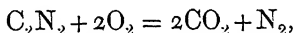


and would be hexamolecular. Van der Staat<sup>2</sup> proved in this case that the first stage is bimolecular, and that when the gases are allowed to diffuse slowly into one another, so that the mutual action takes place in a dilute state, it corresponds sharply to the equation

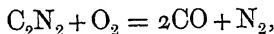


metaphosphoric acid and hydrogen being formed in theoretical quantity.

Smithells and Dent<sup>3</sup> found in the same way for the combustion of cyanogen, represented as a whole by the trimolecular equation

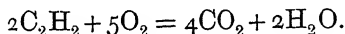


that the first stage of the process is bimolecular,



since the requisite quantity of carbon monoxide is produced.

Bone and Cane<sup>4</sup> found the same to be true for the combustion of acetylene, heptamolecular according to



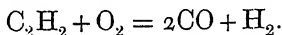
<sup>1</sup> Noyes, *Zeitschr. f. Phys. Chem.* 18. 131.

<sup>2</sup> l. c. 12. 322; *Inaugural Dissertation*, Amsterdam, 1893.

<sup>3</sup> *Journ. Chem. Soc. Trans.* 1894, p. 603.

<sup>4</sup> l. c. 71. 26.

The first stage is again a bimolecular process resulting in formation of carbon monoxide and hydrogen :



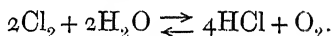
Kinetically the rarity of polymolecular reactions is quite intelligible. The probability of a simultaneous collision between three molecules, and those of specified kinds, is a very small one; so the reaction proceeds, if it is possible at all, by the actions taking place within a single molecule, or on the meeting of two.

### 5. *Relation between the Constants of Equilibrium and of Velocity.*

If the condition of the equilibrium be represented, as on p. 187, by the equation

$$C'_2{}^{n'_2} C''_2{}^{n''_2} \dots = K C'_1{}^{n'_1} C''_1{}^{n''_1} \dots,$$

in which  $K$  is called the reaction constant, a relation is to be found between it and the constant of velocity  $k$ , just considered. The relation follows from the equation if equilibrium without any substances in excess be assumed. By way of example consider



The equation of equilibrium is then

$$C_{\text{HCl}}^4 C_{\text{O}_2} = K C_{\text{Cl}_2}^2 C_{\text{H}_2\text{O}}^2.$$

If now none of the bodies are in excess, i. e. the  $\text{Cl}_2$  and  $\text{H}_2\text{O}$  as well as the  $\text{HCl}$  and  $\text{O}_2$ , in the proportions in which they occur in the reaction, then the following simple relations between the concentrations hold :

$$C_{\text{HCl}} = 4C_{\text{O}_2} \quad \text{and} \quad C_{\text{Cl}_2} = C_{\text{H}_2\text{O}}.$$

We may, however, gain a further simplification by choice of the unit of concentration, taking as unit not the molecular quantity, but the quantity occurring in the reaction, i. e.  $2\text{Cl}_2$ ,  $2\text{H}_2\text{O}$ ,  $4\text{HCl}$ , and  $\text{O}_2$ . Then only two concentrations will come into account, which may be called the con-

centration of the first and second systems respectively, and may be represented by  $C_1$  and  $C_2$ . The equation of equilibrium becomes then

$$C_2^{n_2} = KC_1^{n_1} \quad (1)$$

in which

$$n_2 = n'_2 + n''_2 + \dots$$

and

$$n_1 = n'_1 + n''_1 + \dots$$

It must be observed that this reaction constant is not always the same as the former. For calling the former  $K_1$ , and the latter  $K_2$ , we have

$$n'_1 n'_1 n''_1 n''_1 \dots K_1 = n'_2 n'_2 n''_2 n''_2 \dots K_2.$$

The law of velocity simplifies in the same way to

$$-\frac{dC}{dt} = kC^n,$$

in which the constant  $k$  may differ from that previously used, just as is the case with the reaction-constant. Hence for the two reciprocal reactions, which together lead to equilibrium,

$$-\frac{dC_2}{dt} = k_2 C_2^{n_2},$$

and

$$-\frac{dC_1}{dt} = k_1 C_1^{n_1}.$$

Since now, with the above choice of unit, the increase of concentration of the one system involves an equal decrease of concentration of the other, the actual velocity in the system tending to equilibrium is

$$\frac{dC}{dt} = k_2 C_2^{n_2} - k_1 C_1^{n_1}.$$

For equilibrium this must obviously be zero, so that

$$k_2 C_2^{n_2} = k_1 C_1^{n_1}. \quad (2)$$

By combining (1) and (2) we get

$$K = \frac{k_1}{k_2}.$$

The reaction constant is, therefore, with proper choice of units of concentration, the ratio between the two velocities of reaction.

The same relation may be deduced kinetically in a simple manner, starting from the two opposing velocities, which by their equality lead to the state of equilibrium. The velocities are

$$-\frac{dC_1}{dt} = k_1 C_1^{n_1},$$

and

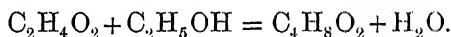
$$-\frac{dC_2}{dt} = k_2 C_2^{n_2},$$

and their equality gives

$$k_1 C_1^{n_1} = k_2 C_2^{n_2},$$

which is nothing else than the equation of the equilibrium with  $\frac{k_1}{k_2}$  instead of  $K$ .

This relation may be tested by an example in which the opposed velocities have been determined experimentally along with the equilibrium. The case is an investigation of Knoblauch<sup>1</sup> on the formation of an ester:



The values of  $n$  are here all alike unity, which much simplifies the theoretical treatment. The velocity of esterification was measured at 25° by bringing 3.001 grams of acetic acid in 50 cub. centimetres together with a mixture in molecular proportion of alcohol and water, containing a little hydrochloric acid, to hasten the reaction. A litre of the liquid contained 1 gram-molecule of acetic acid to 12.756 each of alcohol and water. During the first period of the reaction, when the velocity is moderately constant, i.e. little influenced by change of concentration, and products of reaction,  $k$ , may be calculated, from the velocity of esterification ( $\Delta C_{\text{ester}} : \Delta t$ ):

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 22. 268. See also Küster, l. c. 18. 161.

<i>Time in minutes.</i>	$\Delta C_{ester}$	$\frac{\Delta C_{ester}}{\Delta t}$
0 . . .	0	
44 . . .	0.1327	0.00302
53 . . .	0.1628	0.00307
62 . . .	0.1847	0.00298
70 . . .	0.2128	0.00304

so that on the average

$$\frac{\Delta C_{ester}}{\Delta t} = 0.00303.$$

Since now

$$\frac{dC_{ester}}{dt} = k_1 C_{acid} C_{alcohol},$$

and

$$C_{acid} = 1, C_{alcohol} = 12.756,$$

$$k_1 = \frac{0.00303}{12.756} = 0.000238.$$

The velocity of decomposition of the ester was measured in a liquid containing per litre 1 gram-molecule of ethyl acetate and 12.215 each of alcohol and water, with the same amount of hydrochloric acid as in the previous experiment. The results were :

<i>Time in minutes.</i>	$\Delta C_{acid}$	$\frac{\Delta C_{acid}}{\Delta t}$
0 . . .	0	
78 . . .	0.0777	0.000996
86 . . .	0.0862	0.001003
94 . . .	0.093	0.000989

therefore on the average

$$\frac{\Delta C_{acid}}{\Delta t} = 0.000996.$$

Since now

$$\frac{dC_{acid}}{dt} = k_2 C_{ester} C_{water},$$

and

$$C_{ester} = 1, C_{water} = 12.215,$$

$$k_2 = \frac{0.000996}{12.215} = 0.0000815.$$



The reaction constant  $K$  in the relation

$$C_{ester} C_{water} = K C_{acid} C_{alcohol},$$

which should be equal to  $\frac{k_1}{k_2}$ , was determined from the final condition in the first experiment, where the ester formed reached the maximum amount of 0.7144 gram-molecule per litre. Hence

$$C_{ester} = 0.7144, \quad C_{water} = 12.756 + 0.7144,$$

$$C_{acid} = 1 - 0.7144, \quad C_{alcohol} = 12.756 - 0.7144,$$

and accordingly

$$K = \frac{0.7144 \times 13.4704}{0.2856 \times 12.0416} = 2.84,$$

whilst

$$\frac{k_1}{k_2} = \frac{0.000238}{0.0000815} = 2.92.$$

## 6. Nature of the Influences hindering Reaction.

As we remarked at the beginning, the observed velocity of reaction is to be considered the result of two factors, which have been named the 'moving force' and the 'resistance' respectively. We are now concerned with the latter, and as it cannot be brought under a single point of view, and indeed is of different nature from one case to another, it is convenient to proceed step by step with definite facts.

(a) *The influences hindering physical changes of state.*

(a) *The need of orientation of the molecules.* Considering the two fundamental transformations between solid and liquid on the one hand, of evaporation and condensation on the other, we come across in each a definite factor influencing the velocity.

The essential point with regard to fusion and solidification is that in fusion the resistance is absent, so that the velocity is proportional to the rate at which heat is supplied; in other words, a solid body cannot be heated above its melting point. It is well known that the opposite view put forward by Carnelley for ice is contradicted by experi-

ment, the most powerful sources of heat being unable to raise it above the melting point. On the other hand, we have the known fact that under-cooling of liquids below their freezing point is possible, and that, indeed, measurements of the rate of freezing<sup>1</sup> at given temperatures below the freezing point may be made. The cause of the delay in the latter case is apparently in the necessary orientation of the molecules on freezing, a movement that of course requires time, whereas, on melting, the molecules can stay in place, and only a small change in volume has to be accomplished.

( $\beta$ ) *The need of change of place.* In evaporation and condensation a second factor appears, which regulates the velocity; it is here the movements involved in the different positions in space which the substance has to make, according as it occupies the larger vapour-space or not. The velocity is in this case conditioned by phenomena that belong to the domain of diffusion.

( $\gamma$ ) *Capillary influences.* Yet a third factor has to be discussed in these physical transformations; it is the presence of the first small quantity of the product of transformation, which is necessary at least in solidification and in condensation. The accelerations occasioned in this way belong to the phenomena of capillarity. It may be added that apparently vapour above a certain concentration condenses spontaneously, and liquid below a certain temperature freezes spontaneously. Thus, according to Ostwald<sup>2</sup>, phenol (melting point,  $37.5^{\circ}$ ) cannot be cooled below  $24^{\circ}$  without becoming solid. We may therefore distinguish stable, metastable, and unstable states: only in the latter case does unconditional transformation take place.

( $b$ ) *The influences hindering chemical changes of state.* As physical changes, as compared with chemical, always appear the simpler, so all the 'resistances' we have discovered in the region of physics appear also in chemical

<sup>1</sup> Gernez, *Journ. de Phys.* [2] 2. 159; Tammann, *Zeitschr. f. Phys. Chem.* 23. 326.

<sup>2</sup> l. c. 22. 289.

transformations, showing themselves in the study of velocities as hindrances to the normal process of a reaction.

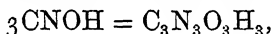
(a) *The need of orientation of the molecules* is, in chemical changes, obviously of more fundamental consequence, and may, as in a mixture of oxygen and hydrogen, lead to states of apparent equilibrium which are not upset by contact with the stable substance. Their analogy in the region of physics may be found in much under-cooled, amorphously solidified liquids, e.g. glasses. Comparing with the physical phenomena of fusion and solidification the corresponding chemical changes, and first the intermediate changes of crystalline forms, e.g. of sulphur, one characteristic feature is that rhombic sulphur can exist above the temperature of conversion, whereas solids cannot be heated above their melting point. The explanation is that, in the first case, the system formed above the temperature of conversion requires a definite molecular orientation. In the second place, it may be noted that such changes of crystalline form go quickly in soft bodies, like carbon hexachloride ( $\text{C}_2\text{Cl}_6$ ), ammonium nitrate, and so on, but in harder substances meet with resistance. Even the reciprocal conversions of sulphur, especially the change back into the rhombic form, in the neighbourhood of the temperature of conversion, proceed very slowly (p. 26), and in general can only be observed by the aid of a solvent, which clearly helps the necessary processes of deorientation and orientation. Further, below the temperature of conversion the process is more rapid on account of the increased 'moving force'; but on further cooling, below  $0^\circ$ , the resistance again gets the upper hand<sup>1</sup>. So too, in the region of minerals, we find countless forms (of every dimorphic substance at least one form) which stay indefinitely in a state of apparent equilibrium, e.g. arragonite, although at ordinary temperatures calcite is the stable form of calcium carbonate.

( $\beta$ ) *The need of change of place.* In case of reactions in

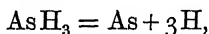
<sup>1</sup> Ruys, *Recueil des trav. Chim. des Pays-Bas*, III. I.

which the mutual action of several molecules is required, the speed with which these move relatively to one another will obviously be a factor in their course. The solvent or medium in which the reaction goes on may be of influence, in this respect, and its viscosity must be considered as of the first importance. But as the solvent has another action as well, the results in this connexion will be detailed later.

( $\gamma$ ) *Capillary influences.* These show themselves in the region of chemistry as of physics, in that the presence of a substance favours its further formation, and in some circumstances is required to make that possible, as in crystallizing out supersaturated solutions, and in the mutual conversion of different crystalline forms. A second point has specially to be attended to in gaseous reactions: local condensation due to capillary action has an accelerating effect on reactions which are accompanied by decrease of volume, i.e. on polymolecular reactions. Thus; e.g., in the trimolecular formation of cyamelide from cyanic acid,



the layer of cyamelide forming on the walls of the vessel has a greatly accelerating effect, whilst in the monomolecular decomposition of arsine,



the layer of arsenic formed exercises hardly any noticeable influence.

( $\delta$ ) *Hindering influences characteristic of chemical change.* From the molecular-mechanical point of view, chemical change, as we have remarked, has, in common with physical change of state, that movements in space are only necessary in the case of polymolecular reactions, as with evaporation and condensation; that in changes taking place in solids, orientation of the molecules is necessary, as in solidification; and that, in the latter case especially, capillary influences, e.g. presence of the substance to be formed, may make themselves felt. All these mechanical necessities correspond to influences that stand in the way

of the process—resistances, that is, which reduce the rate of reaction, and may even stop the reaction altogether.

There is, however, amongst chemical phenomena, a whole series of cases in which bodies or systems of bodies retain their condition although the hindering influences just discussed are absent. This is most strikingly shown in isomerism. Consider a pair of isomers, such as fumaric and maleic acid, of which the latter, on warming, on presence of a trace of bromine and illumination, is converted into the former, and is therefore to be regarded as the less stable. Remove all the resistances, as e.g. by bringing maleic acid in solution into contact with fumaric, and still the maleic acid remains what it was, and it can hardly be supposed that in all such cases there is a velocity of reaction, but excessively small. Molecular-mechanically considered then, in addition to molecular orientation and displacement, a displacement, or exchange of the atoms, is of the first importance for chemical changes; and that may just as well be stopped by resistances, as glass in its conversion to the crystalline state, i. e. to Réaumur porcelain.

Apart from such considerations, it is important that many experimental results, especially recent ones, show that every substance and every complex of substances can remain in a state of apparent equilibrium, sharply defined by pressure and temperature. The oldest observations on this point refer to the phosphorescence, i. e. the oxidation of phosphorus. Davy found that above a certain pressure of oxygen the phosphorescence ceases, and Joubert<sup>1</sup> put this limit more exactly into its connexion with temperature, and found that phosphorescence sets in below the following limits of pressure:—

*Temperature. Pressure of Oxygen.*

1.4°	355 mm.
3°	387 "
4.4°	408 "
5°	428 "
6°	460 "
8.9°	519 "

*Temperature. Pressure of Oxygen.*

9.3°	538 mm.
11.5°	580 "
14.2°	650 "
18°	730 "
19.2°	760 "

<sup>1</sup> *Thèse sur la Phosphorescence du Phosphore.* Paris, 1874.

This result, graphically represented by aid of two axes, the vertical for pressure, the horizontal for temperature (Fig. 62), gives a nearly straight line, dividing the diagram into an upper part in which oxidation does not, and a lower in which it does take place. The former is therefore the region of so-called apparent (or false) equilibrium.

Similar results have lately been obtained by Hélier<sup>1</sup> and Pélabon<sup>2</sup>. The former finds that between certain limits of temperature the conversion of oxygen and hydrogen into water, and of carbon monoxide and oxygen into carbon

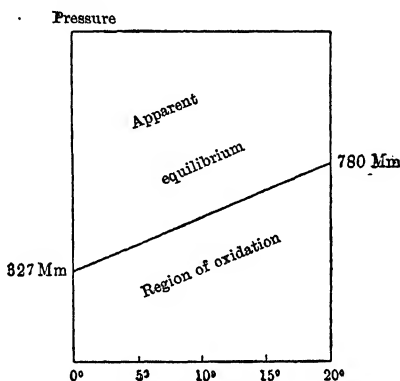


FIG. 62.

dioxide, is limited, and that, with regard to the first case, however long heated in contact with glazed porcelain, only the following percentage is converted at the temperature stated:—

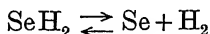
Temperature.	Limit.	Temperature.	Limit.
180°	0.04%	433°	30.81%
200°	0.12%	498°	56.38%
239°	1.3%	620°	84.52%
260°	1.6%	637°	85.65%
331°	9.78%	825°	96.1%
376°	25.11%	845°	Explosion.
416°	35.7%		

Pélabon found that the formation and decomposition of seleniuretted hydrogen, which above 325° lead to a definite

<sup>1</sup> *Comptes Rendus*, 122. 566.

<sup>2</sup> *l. c.* 124. 360.

mixture of the compound and its elements, indifferently whether the former or the latter serve as starting point, below  $325^{\circ}$  do not lead to the same final state. The equilibrium



is, according to the laws previously developed, governed by the condition

$$\frac{C_{\text{SeH}_2}}{C_{\text{H}_2}} = \frac{p_{\text{SeH}_2}}{p_{\text{H}_2}} = \frac{p_2}{p_1} = K.$$

The author accordingly gives for each observed temperature the final value of  $\frac{p_2}{p_1 + p_2}$  reached.

Temperature.	Time of heating.	Final value of $\frac{p_2}{p_1 + p_2}$ .	
	Hours.	Formation.	Dissociation.
$300^{\circ}$	212	0.124	0.172
$300^{\circ}$	322	0.127	0.17
$315^{\circ}$	196	0.164	0.185
$315^{\circ}$	320	0.1625	0.1801
$325^{\circ}$	175	0.187	0.193
$325^{\circ}$	213	0.1882	0.192

It should be noted that the limits so defined, which bound the region of apparent equilibrium, are by no means fixed. In the phosphorescence of phosphorus, e.g., they depend on the amount of moisture present. The combination of oxygen and hydrogen, again, is ultimately dependent on the substance with which the gases are in contact. Thus, Mitscherlich<sup>1</sup> gives the temperature of explosion in glass vessels as  $674^{\circ}$  instead of  $845^{\circ}$ .

Thermo-dynamically the existence of apparent equilibria may perhaps mean that the total work a reaction can give out does not correspond to the moving force at each stage of the reaction. It would do so if the same thing happened from moment to moment. That is obviously not the case during an orientation, and it is quite possible that a total positive expenditure of work is associated with a negative during parts of the process. These would then correspond

<sup>1</sup> *Berl. Ber.* 26. 164. See also V. Meyer, l. c. p. 428.

to an equal number of forms of apparent equilibrium, i. e. polymorphic states, or isomers.

*7. General Conclusions with regard to the Determination of Velocity of Reaction.*

With the numerous influences that, we have seen, make themselves felt in the velocity of reaction, it is easily understood that the normal course of a reaction, as expressed by the equation

$$-\frac{dC}{dt} = kC_I^{n_I}C_{II}^{n_{II}}\dots,$$

only appears undisturbed when all the factors are taken into account.

In the first place, we have the fundamental condition that the above equation is only true for considerable dilution (practically tenth-normality).

Next, however, come the disturbances produced by the process itself or its products, usually appearing as an acceleration due to the presence of the products of reaction. These influences may often be avoided by the use of a solvent, whose overpowering quantity often sufficiently overcomes the influence of new products.

For these reasons measurements of reaction in gases have had the least result, as the products are then in a position to exercise their full effect. The difficulty has so far only been overcome for the cases of slow dissociation of arsine and phosphine (p. 190), and the formation and dissociation of hydriodic acid (p. 188).

§ 2. EMPIRICAL RESULTS IN THE STUDY OF VELOCITY OF REACTION.

We have now to consider the various observations connected with velocity of reaction, which have not yet been arranged under definite laws. Still a choice has to be made, and only those facts to be brought forward which,



so far as can at present be seen, are not in too loose connexion with what has been arranged in order. We have accordingly restricted ourselves to the following four sections:—

A. Influence of the surroundings and the medium on velocity of reaction.

B. Influence of temperature.

C. Influence of pressure.

D. Waves of reaction.

Since now we are mainly concerned with the empirical material, the facts will be brought forward first, and moderately fully, while previously they served chiefly to develop or to verify certain generalizations. Afterwards we may develop the theory as far as possible in the direction indicated by those facts. A common tendency will become prominent, that of applying the laws of equilibrium, and especially thermo-dynamics, in the service of the study of velocity of reaction.

#### A. Influence of the Surroundings and the Medium on Velocity of Reaction.

##### 1. *Influences which alter the Velocity of Reaction, but not the Equilibrium.*

(a) *Contact effects.* The peculiarity of contact action is that certain substances accelerate a reaction, or even start it, apparently without any change in themselves; at least, after the reaction is over the substances in question are found in the same quantity and the same state, and can accordingly effect the reaction to an unlimited extent.

The fundamental rule, empirically and theoretically, on such actions is that the velocity is altered by them, but not the condition of equilibrium. Lemoine<sup>1</sup>, e.g., found 0.186 for the proportion of hydriodic acid dissociated at 350° without spongy platinum, while Hautefeuille found

<sup>1</sup> *Ann. de Chim. et de Phys.* 1877 [5], 12.

0.19 in presence of that substance; Ditte<sup>1</sup> found on the whole that the same is true of the formation of seleniuretted hydrogen in presence and absence of pumice-stone; at high temperature (440°), when the phenomena of apparent equilibrium (p. 210) do not interfere, he found in two similar experiments, without and with pumice-stone, 45.2 and 46.82 formed respectively.

Theoretically too, assuming that contact actions affected the equilibrium, we should come upon a perpetuum mobile, by working alternately with and without the contact substance; the conversion might thus be carried backwards and forwards indefinitely, and so work be accomplished in any way, without fall of temperature, in contradiction to the laws of thermo-dynamics.

From the inability of such contact substances to effect a displacement of equilibrium, there follows immediately that if the contact substance increases the velocity of one of the two reactions leading to equilibrium, it must do so for the other too. Thus, if decomposition of hydriodic acid becomes more rapid by the action of spongy platinum, the same must be true for the formation of hydriodic acid, which has in fact been observed.

Molecular-mechanically considered, contact actions may probably be compared with that of a solvent in the mutual conversion of different crystalline forms, in the fact that they remove the hindrances to the requisite displacement of the atoms. It is therefore to be expected that they should alter the limits of apparent equilibrium which are connected with such hindrances (p. 210). Further, the condensation on the surface of bodies producing constant effects—mostly porous bodies—is essential to the explanation; it is indeed comparable to the effect of a local very high pressure, which in spongy platinum is combined with the immediate proximity of a good conductor (see p. 185).

(b) *Action of traces of moisture.* Whilst Bunsen and Roscoe found that the rate of formation of hydrochloric

<sup>1</sup> *Comptes Rendus*, 1872, p. 980.

acid from hydrogen and chlorine by light is greatly reduced by the presence of quite small traces of gas, not long since<sup>1</sup> attention was again drawn to action of moisture, also in mere traces, on reactions in which the complicating factor of light plays no part. Myers found that carbon will not burn in dry oxygen, and Dixon showed that a carbon-monoxide-oxygen mixture, dried over phosphorus pentoxide, loses its explosibility; and Baker added a whole series of similar facts, in various connexions, from which it appears that many reactions are greatly accelerated, or even first become possible, through traces of moisture. As an example, we may quote the failure to produce  $\text{NO}_2$  by combination of dry  $\text{NO}$  and oxygen.

Since here again we have to do with quite small quantities, which reappear after the equation unchanged, the same considerations hold as for contact action (p. 214), with the exception of the localization occurring in it. The same fundamental rule is therefore applicable; the influences in question do not affect the state of equilibrium, and must therefore alter the two reciprocal reactions in the same sense and to the same degree (change the velocity constants in the same ratio). Baker showed that in a striking manner for the combination and separation of hydrochloric acid and ammonia. Fully dried, the two gases come together without contraction or clouding, whilst, on the other hand, dry ammonium chloride on evaporation gives off unchanged ammonium chloride vapour. Moisture leads in the first case immediately to combination; in the latter, as is well known, to dissociation.

With regard to the explanation, we may say that though the accelerating influence of moisture has been shown in more than twenty reactions of most various kinds, it can hardly be regarded as a specifically chemical action. Baker<sup>2</sup> suggests that the electric conductivity due to

<sup>1</sup> Dixon, *Phil. Trans.* 1884, p. 629; Baker, *Chem. Soc. Trans.* 1885, p. 349; 1894, p. 612; *Proc.* 1893, p. 129; *Proc. Roy. Soc.* 45. 1.

<sup>2</sup> See also J. J. Thomson, *Phil. Mag.*, Oct. 1893.

traces of moisture (p. 185), and also the exceptionally high dielectric constant of water, to be referred to later, may be closely connected with the phenomenon<sup>1</sup>.

2. *Influences which affect both Velocity of Reaction and Equilibrium.*

If the surroundings in which a reaction takes place are changed, either by adding some other substance to the solvent, or entirely replacing the solvent by another, then—chemical action being excluded—we may again speak of contact action, in the sense that the added substance or the new solvent remains unchanged after the reaction is over. The action is, however, so far different that it is no longer due to the influence of traces, nor is it local, but is due to influences that may alter the internal molecular state of the reacting substances, as is shown, e. g., by the alteration of optical activity produced by a solvent<sup>2</sup>. Accordingly change of equilibrium is possible, is probable, and indeed actually occurs. Whilst then, in the preceding case of contact action in the stricter sense, we had only to do with changes of velocity affecting the two reciprocal reactions to the same extent, we are now concerned with influences that make themselves felt on the equilibrium, and accordingly change the reciprocal velocities of reaction to different extents, and in such a way as to answer to the displacement of equilibrium. We will keep this double character in view, and first discuss the observations on change of velocity, afterwards their relation to the state of equilibrium.

(a) *Change of velocity due to the addition of soluble substances.* The influence especially of neutral salts on the velocity of chemical reactions has been repeatedly the subject of investigation. Thus Ostwald<sup>3</sup> found that the

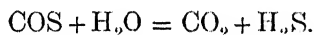
<sup>1</sup> Nernst, *Zeitschr. f. Phys. Chem.* 13, 531; Brühl, l. c. 18, 514.

<sup>2</sup> Landolt, *Das optische Drehungsvermögen*, 1897, p. 146.

<sup>3</sup> *Journ. f. Prakt. Chem.* (New Series), 23, 209.

action of hydrochloric and nitric acids on calcium and zinc oxalate is accelerated by the addition of salts, most by K-salts, less by Na- and  $\text{NH}_4$ -, which are about equal in their action, and least by Mg-salts. H. Trey<sup>1</sup> showed that metallic chlorides hasten the catalysis of methyl acetate by hydrochloric acid. The accelerating influence proved to be the greater the less the atomic weight of the metal. The rate of saponification by sulphuric acid was reduced by addition of sulphates, and here the reducing effect increased with the atomic weight. Arrhenius<sup>2</sup> studied the action of neutral salts on the rate of saponification of ethyl acetate by bases, and found throughout a reducing effect. It is the greatest for KI, and successively less for  $\text{KNO}_3$ , KBr, KCl; sodium salts reduce the velocity more strongly, and barium still more. Finally, Spohr<sup>3</sup> and Arrhenius<sup>4</sup> proved that the rate of inversion of cane sugar in presence of acids is increased by addition of neutral salts.

All the experiments mentioned are complicated by an effect that is to be expected from the simultaneous presence of acids and bases—either a reaction between them, or a change in the degree of dissociation (p. 120). In that respect the conversion of carbon oxysulphide by water, studied by Buchböck<sup>5</sup>, is simpler:



The velocity constant  $k$  of the reaction, which is monomolecular (on account of the presence of water in great excess, p. 200), is for  $24.94^\circ$  (time in minutes) given in the following table; the acids and salts in question were applied in normal solution:—

<sup>1</sup> *Journ. f. Prakt. Chem.* 34. 353.

<sup>2</sup> *Zeitschr. f. Phys. Chem.* 1. 110.

<sup>3</sup> *l. c.* 2. 194.

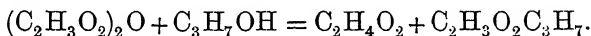
<sup>4</sup> *l. c.* 4. 226.

<sup>5</sup> *l. c.* 23. 123. Hydrogen peroxide is a suitable subject of investigation, since its conversion is effected by acids, bases, and salts, and it keeps perfectly, e.g., in ethereal solution (*Spring, Acad. de Belg.* 30. 32).

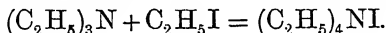
A. Salts.	$10^6k$ 2.30259	Viscosity.	B. Acids.	$10^6k$ 2.30259	Viscosity.
KNO <sub>3</sub> . . .	630	0.9753	Water . . .	527	1
KCl . . .	609	0.9872	CH <sub>3</sub> COOH . .	508	1.1131
NH <sub>4</sub> Cl . . .	579	0.9884	CHCl <sub>2</sub> COOH	488	1.2649
NaNO <sub>2</sub> . . .	540	1.0655	H <sub>2</sub> SO <sub>4</sub> . . .	469	1.0898
Water . . .	527	1	HCl . . .	384	1.0671
NaCl . . .	529	1.0973	HBr . . .	358	1.032
BaCl <sub>2</sub> . . .	514	1.1228			
NaBr . . .	504	1.0639			
SrCl <sub>2</sub> . . .	497	1.1411			
CaCl <sub>2</sub> . . .	481	1.1563			
HgCl <sub>2</sub> . . .	460	1.2015			
LiCl . . .	432	1.1423			

By the side of the velocity constants the viscosities are given, also as measured by Buchböck, they being one of the factors to which the velocity of reaction is related. The acids retard, the salts partly accelerate. The retarding effect of the former is, with the exception of dichloroacetic acid, greater the smaller the viscosity. In salts also the velocity increases as the viscosity decreases, with the exception of strontium and lithium chloride and sodium bromide.

(b) *Change of velocity due to change of solvent.* To this section belong especially the experiments of Menshutkin on the action of acetic anhydride on isopropyl and isobutyl alcohol<sup>1</sup>:



The velocity was determined at 100°, time being measured in minutes; a corresponding investigation was carried out, also at 100°, with triethylamine and ethyl or propyl iodide<sup>2</sup>:



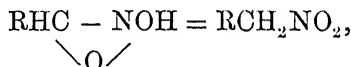
The following table contains the essential results, showing the influence on the velocity of the solvent mentioned in the first column. It is seen to be very considerable; e.g. the velocity of formation of tetraethyl ammonium iodide in hexane and in acetophenone respectively was found to be 0.00018 and 0.1294, that is, in the ratio 1:720. After the velocities are placed the data with regard to

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 1. 611.

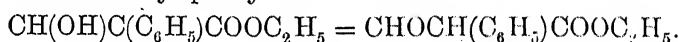
<sup>2</sup> l. c. 6. 41.

viscosity, and also the dielectric constants of the different solvents, which are commonly thought to stand in a close relation to the velocities. The relations seem, however, to be only distant.

To complete the list of data, we must mention that Hantzsch finds the action of the solvent on the conversion of isonitroso- into nitroso-bodies,



similar; and Wislicenus too for the conversion of the isomeric formyl-phenyl-acetic ethers:



	<i>Acetic anhydride.</i>		$(\text{C}_2\text{H}_5)_3\text{N}$		<i>Viscosity</i> <sup>1</sup> .	<i>Dielectric</i> <sup>2</sup> constant.
	<i>Iso-butyl alcohol</i> (100°).	<i>Iso-propyl alcohol</i> (100°).	$\text{C}_2\text{H}_5\text{I}$ (100°).	$\text{C}_6\text{H}_7\text{I}$ (100°).		
Hexane . . . .	0.0877	0.0307	0.00018	—	0.00315 (20°)	1.86 (12.3°)
Heptane . . . .	—	—	0.000235	—	0.00449 (20°)	—
Xylene . . . .	0.051	0.0196	0.00287	—	—	2.57 (17°)
Benzene . . . .	0.0401	0.014	0.00584	0.000945	0.00654 (20°)	2.26 (19°)
Propyl chloride .	—	—	0.0034	—	—	—
Chlorobenzene . .	—	—	0.0231	—	—	—
Bromobenzene . .	—	—	0.027	0.0057	—	—
$\alpha$ -bromnaphthalene	—	—	0.1129	—	—	—
Ethyl ether . . . .	—	—	0.000757	—	0.0025 (20°)	4.36 (18°)
Ethylisoamyl ether	—	—	0.00063	—	—	—
Phenetol . . . .	—	—	0.0212	—	0.01286 (20°)	—
Anisol . . . . .	—	—	0.0403	—	—	—
Ethyl acetate . .	—	—	0.0223	—	0.00561 (20°)	5.85 (20°)
Isobutyl acetate .	—	—	0.00577	—	0.00718 (20°)	5.27 (19.5°)
Ethyl benzoate . .	—	—	0.0259	—	0.02285 (20°)	6.04 (19°)
Isobutyl alcohol .	—	—	0.0258	—	0.04112 (20°)	6.1 (18°)
Ethyl alcohol . .	—	—	0.0366	—	0.01211 (20°)	21.7 (15°)
Allyl alcohol . .	—	—	0.0433	—	—	20.6 (21°)
Methyl alcohol . .	—	—	0.0516	—	0.00623 (20°)	32.5 (16°)
Benzyl alcohol . .	—	—	0.133	—	0.0569 (20°)	10.6 (21°)
Acetone . . . . .	—	—	0.0608	0.0116	0.01716 (20°)	21.8 (15°)
Acetophenone . .	—	—	0.1294	0.0292	—	15.5 (17°)

<sup>1</sup> Landolt and Börnstein.

<sup>2</sup> Id.; Thwing, *Zeitschr. f. Phys. Chem.* 14. 292; Drude, l. c. 23. 308.

The velocity diminishes successively for

Water—alcohol—ether—benzene—chloroform.

The dielectric constants are respectively :

75.5      21.7      4.36      2.26      4.95

In the action of triethylamine on ethyl iodide the order is :

Alcohol—benzene—ether.

(c) *Change of equilibrium due to the solvent.* It has already been remarked that the change that the velocity may suffer through change of solvent is connected with the displacement of equilibrium which that change may bring about. On the whole, then, we may divide the change of velocity into two parts, of which one, acting equally on the two reciprocal reactions, may be compared with the contact actions already discussed, and may depend on any physical properties of the solvent. The other part, acting differently on the reciprocal reactions, must be of a specific nature, and be connected with some interaction between the solvent and the reacting bodies. This division of the effect of the solvent may be sharply formulated by means of the conditions of equilibrium.

If for two solvents—say carbon disulphide and water—the conditions of equilibrium in any case are

$$K_a = \Sigma n \log C_a \quad \text{and} \quad K_b = \Sigma n \log C_b,$$

then we have already (p. 113) discussed how these reaction constants may be derived from that in the gaseous state,

$$K = \Sigma n \log C,$$

by means of the absorption coefficients. But they may also be related to one another by considering only what happens when the solutions, in carbon disulphide and water, of the substances in equilibrium are shaken together. A displacement occurs until the double condition is satisfied, given by the law of sharing and the condition of equilibrium. The former states that for dilute solution,



if the molecular state of the substances in question is the same in the two solvents, a fixed ratio holds between the concentrations for each substance, which is called the coefficient, or ratio of sharing. This ratio is, however, for slightly soluble substances, proportional to the solubility ( $S$ ), and thus between the conditions of equilibrium there exists the simple relation

$$\frac{C_a}{C_b} = \frac{S_a}{S_b}.$$

Hence we have now

$$K_a - K_b = \Sigma n \log C_a - \Sigma n \log C_b = \Sigma n \log \frac{C_a}{C_b} = \Sigma n \log \frac{S_a}{S_b},$$

or

$$K_a - \Sigma n \log S_a = K_b - \Sigma n \log S_b = \mathbf{K}.$$

We thus get a new reaction constant  $\mathbf{K}$ , independent of the solvent, and which may be calculated in the following way:—

$$\mathbf{K} = K - \Sigma n \log S = \Sigma n \log \frac{C}{S}.$$

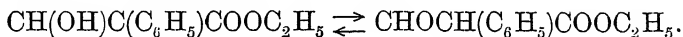
i. e. the same function of the concentrations appears, only the unit of concentration is no longer the gram-molecule per litre, but the concentration of the saturated solution. A very simple relation unites this new constant to the temperature of conversion (p. 64). If two condensed systems are in equilibrium, as is the case at that temperature, they are so also in presence of a solvent. The saturation concentration, therefore, also corresponds to equilibrium. But then

$$\mathbf{K} = 0.$$

The new relation thus connects all the states of equilibrium in solution with the temperature of conversion, and also with equilibrium in the gaseous state,  $S$  being the concentration corresponding to the maximum vapour pressure.

This conclusion may be elucidated by means of an example. Let us take the simplest case of a mutual con-

version of isomers, like that (mentioned on p. 220) of the isomeric formyl-phenyl-acetic ethers:



Then the general condition of equilibrium is

$$\Sigma n \log C = K,$$

corresponding to

$$\log \frac{C_1}{C_2} = K,$$

where  $C_1$  and  $C_2$  are the concentrations which correspond to equilibrium in any solvent. These concentrations are equal to those ( $S_1$  and  $S_2$ ) of a solution saturated with both isomers at the temperature  $T$  at which the two are in equilibrium with one another, i. e. at the temperature of conversion, and accordingly

$$\log \frac{S_1}{S_2} = K_T = \log \frac{C_1}{C_2}.$$

The above relation states then that while the reaction constant  $K$  varies from one solvent to another, by choosing the saturation concentration as unit we get a reaction constant  $K$  given by

$$\log \frac{C_1}{S_1} - \log \frac{C_2}{S_2} = K,$$

which is independent of the solvent, and at the temperature of conversion is zero.

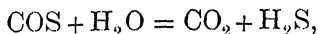
The expression obtained in this way may now be introduced into the region of velocities. The medium exercises, we have seen, a double influence, one connected with the displacement of equilibrium, while the other is perhaps to be referred to some physical property of the medium. But the influence on equilibrium vanishes if we choose saturation as the unit of concentration. It is then natural, in judging of the effect on the velocity, to choose saturation as the unit, and instead of the value expressed in terms of the constant  $k$ ,

$$- \frac{dC_I}{dt} = k C_I^{n_I} C_{II}^{n_{II}} \dots,$$

to choose a constant  $k$  defined by the equation

$$-\frac{dC_I}{dt} = k \left(\frac{C_I}{S_I}\right)^{n_I} \left(\frac{C_{II}}{S_{II}}\right)^{n_{II}} \dots$$

Applying to the case considered on p. 218 of decomposition of carbon oxysulphide,



which was followed out in water and aqueous solutions, it would be necessary to determine the absorption coefficients ( $A$ ), and to compare the value of  $k$  derived from the equation

$$-\frac{dC}{dt} = k \frac{C}{A}.$$

Then perhaps the relation to the viscosity would become clearer.

We must now state what is known experimentally with regard to displacement of equilibrium. Observations on the molecular magnitudes of bodies which may form double molecules in solution, and on electrolytic dissociation, are of essential importance with regard to the influence of the solvent. As to the first point, the carboxylic acids, the oxims, alcohols, &c., i. e. especially bodies containing hydroxyl, dissolved in hydrocarbons, chloroform, and carbon disulphide show double molecular weight. The molecular complexes break up, on the contrary, when those substances are dissolved in water; alcohols, ethers, esters, ketones, and phenols also act, though less completely, as dissociating media<sup>1</sup>. On the other hand, water shows the well-known phenomenon of electrolytic dissociation with salts, acids, and alkalis; next to it stand methyl alcohol and formic acid; other liquids, so far as is known, possess this property only in a very slight degree<sup>2</sup>. Nernst<sup>3</sup> associates both actions with the dielectric constant,

<sup>1</sup> See among others Beckmann, Paterno, Auwers, *Zeitschr. f. Phys. Chem.* 18. 595; 21. 337.

<sup>2</sup> Kablukoff, l. c. 4. 429; Wakemann, l. c. 11. 63; Zelinsky, l. c. 21. 49.

<sup>3</sup> l. c. 13. 534.

which has the highest known value (75.5) for water, the next highest (62) for formic acid, &c. Brühl<sup>1</sup> brings the facts into connexion with the oxygen-content, and then refers them to free oxygen affinities. In fact, according to Thwing<sup>2</sup>, the dielectric constant is closely connected with the content of oxygen. According to the preceding discussion, it is hardly to be expected that a single physical property should be decisive of these relations of equilibrium. Zanninovich-Tessarini<sup>3</sup> concludes from a research on formic acid that 'formic acid is really a solvent that produces a very strong electrolytic dissociation of salts, and that is in agreement with its high dielectric constant, but the acids that dissociate almost completely in water do not do so at all in formic acid; indeed they seem to show in it a greater molecular aggregation than corresponds to the simple molecules. Hence it seems that a high dielectric constant in the solvent is not always in itself sufficient to produce and to favour electrolytic dissociation. Moreover the fact is general that the order of dissociation of different substances is not identical in different solvents, which shows that the phenomenon of ionization cannot depend absolutely on a single physical property of the solvent; at the same time it does not exclude the inference that the dielectric constant is the most important factor.'

The essential point with regard to velocity of reaction is that the loosening or dissociating influence of the solvent must increase the velocity of any reaction which leads to a break up of the molecule at the point thus loosened.

## B. Influence of Temperature on Velocity of Reaction.

### 1. *Experimental Data.*

*Measurement and expression of the influence of temperature.* With regard to the influence of temperature on velocity of reaction, it must first be settled, whether and

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 18. 514.

<sup>2</sup> *l. c.* 14. 298.

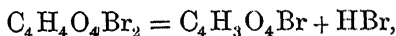
<sup>3</sup> *l. c.* 19. 259.

when the reaction in question goes in such a way as to satisfy the relation between time and extent of reaction expressed by

$$-\frac{dC_I}{dt} = kC_I^{n_I}C_{II}^{n_{II}}.$$

Only when this preliminary problem is solved can  $k$  be determined for different temperatures, and so a clear view obtained of the effect of temperature.

As an example, let us choose the conversion of dibrom-succinic acid in aqueous solution which takes place according to the equation



and accordingly satisfies the monomolecular equation

$$-\frac{dC}{dt} = kC.$$

The values of  $k$  calculated from the integrated equation in the way previously explained (p. 191) are, at different temperatures, those shown in the following table:—

<i>Temperature.</i>	<i>k (time in minutes).</i>	<i>Temperature.</i>	<i>k (time in minutes).</i>
15°	0.00000967	70.1°	0.00169
40°	0.0000863	80°	0.0046
50°	0.000249	89.4°	0.0156
60.2°	0.000654	101°	0.0318

In the first place, these numbers give numerical expression to the known fact that the velocity increases with temperature. They show, moreover, how great the effect of temperature is, since a rise of 86° increases the velocity from 0.00000967 to 0.0318, i.e. more than three thousand times. In the second place, the numbers again show the leading empirical relation between temperature and velocity, which is that equal rises of temperature are accompanied by equal ratios of velocity.

We will next add another empirical relation—that the ratio of velocities for a given interval of temperature mostly differs little from reaction to reaction, and for 10°,

for which in the case of dibromsuccinic acid between  $40^{\circ}$  and  $50^{\circ}$  it is  $\frac{0.000249}{0.0000863} = 2.88$ , it often lies between two and three.

To test this empirical relation for different reactions, since measurements are not always to be had for  $10^{\circ}$  intervals, we must next introduce the equation which that relation between temperature and velocity yields, viz.

$$\log_{10} k = a + bt,$$

from which the ratio for a temperature difference of  $10^{\circ}$  comes to

$$\frac{k_{t+10}}{k_t} = 10^{10b}.$$

Thus, e. g., in the saponification of ethyl acetate by soda the numbers found for  $k$  (time in minutes) are

$$\begin{array}{lll} \text{at } 9.4^{\circ} & . & . & k = 2.307, \\ \text{,, } 44.94^{\circ} & . & . & k = 21.648; \end{array}$$

hence

$$\log 2.307 = a + 9.4 b \text{ and } \log 21.648 = a + 44.94 b,$$

whence

$$b = 0.0274 \text{ and } \frac{k_{t+10}}{k_t} = 1.89.$$

The mean velocity ratios so found are collected in the table on the following page.

By far the greater number of reactions double or treble their velocity for  $10^{\circ}$  rise of temperature. Moreover the quantity of carbon dioxide respired by wheat, lupines, and syringa shows between  $0^{\circ}$  and  $25^{\circ}$  an increase amounting to two and a half fold for each  $10^{\circ}$ .

The only case in which the increase is much greater than threefold is the enzyme action mentioned, viz. the dissociation of salicin by emulsin.

Only the dissociation of phosphine and arsine show much less than a doubling of velocity. That is perhaps connected with the high temperature at which the observations

were made, since in the great majority of cases yet observed the velocity ratio for  $10^\circ$  falls off with rise of temperature<sup>1</sup>.

Reaction <sup>2</sup> .	Velocity (time in minutes).		Ratio for $10^\circ$
$\text{PH}_3 = \text{P} + \text{H}_3$ <sup>3</sup> . . . . .	$k_{310} = 0.000006$	$k_{512} = 0.00031$	1.2
$\text{AsH}_3 = \text{As} + \text{H}_3$ <sup>4</sup> . . . . .	$k_{256} = 0.00035$	$k_{367} = 0.0034$	1.23
$\text{C}_2\text{H}_3\text{O}_2\text{C}_2\text{H}_5 + \text{NaOH}$ <sup>5</sup> . . . . .	$k_{9.4} = 2.307$	$k_{44.94} = 21.648$	1.89
$\text{C}_2\text{H}_3\text{ONH}_2\text{Aq}$ <sup>6</sup> . . . . .	$65^\circ$ to $100^\circ$	. . . . .	2.12
$\text{KClO}_3 + \text{FeSO}_4 + \text{H}_2\text{SO}_4$ <sup>7</sup> . . . . .	$k_{10} = 1$	$k_{32} = 7.15$	2.44
$\text{C}_2\text{H}_2\text{ClO}_2\text{Na} + \text{NaOH}$ <sup>8</sup> . . . . .	$k_{70} = 0.000822$	$k_{150} = 0.217$	2.54
$\text{C}_2\text{H}_3\text{ClO}_2\text{Aq}$ <sup>8</sup> . . . . .	$k_{80} = 0.0000222$	$k_{130} = 0.00237$	2.55
$\text{C}_4\text{H}_4\text{O}_4\text{Br}_2\text{Aq}$ <sup>9</sup> . . . . .	$k_{15} = 0.00000967$	$k_{101} = 0.0318$	2.65
$\text{CH}_2\text{OHCH}_2\text{Cl} + \text{KOH}$ <sup>10</sup> . . . . .	$k_{24.5} = 0.68$	$k_{43.6} = 5.23$	2.87
$\text{CH}_3\text{CHOHCH}_2\text{Cl} + \text{KOH}$ <sup>10</sup> . . . . .	$k_{24.5} = 4.9$	$k_{43.6} = 31$	2.68
$(\text{CH}_3)_2\text{COHCH}_2\text{Cl} + \text{KOH}$ <sup>10</sup> . . . . .	$k_{24.5} = 173$	$k_{43.6} = 1100$	2.66
$(\text{CH}_3)_2\text{COHCHClCH}_3 + \text{KOH}$ <sup>10</sup> . . . . .	$k_{24.5} = 193$	$k_{43.6} = 940$	2.7
$\text{HPO}_3\text{Aq}$ <sup>11</sup> . . . . .	$0^\circ$ to $61^\circ$	. . . . .	3
$\text{NaOC}_2\text{H}_5 + \text{CH}_3\text{I}$ <sup>12</sup> . . . . .	$k_0 = 0.00336$	$k_{30} = 2.125$	3.34
Diazoamido- to amidoazo-benzene <sup>13</sup> . . . . .	$k_{25} = 0.0001$	$k_{55} = 0.0042$	3.48
Inversion of sugar <sup>14</sup> . . . . .	$k_{25} = 0.765$	$k_{55} = 35.5$	3.63
$\text{COS} + \text{H}_2\text{O}$ <sup>15</sup> . . . . .	$k_{16.05} = 0.00031$	$k_{40.14} = 0.00815$	3.68
Respiration of plants <sup>16</sup> . . . . .	$0^\circ$ to $25^\circ$	. . . . .	2.5
Fermentation <sup>17</sup> . . . . .	$60^\circ$ to $75^\circ$	. . . . .	7.14

It follows from the rapid increase of velocity with temperature that comparatively few reactions are suitable

<sup>1</sup> The only known exception so far is the dissociation of arsine,  $k_{256} = 0.00035$ ;  $k_{311} = 0.00084$ ;  $k_{367} = 0.0034$ . But these numbers require confirmation.

<sup>2</sup> The unit of concentration is the quantity in grammes expressed by the formula per litre.

<sup>3</sup> Kooy, *Zeitschr. f. Phys. Chem.* 12. 155.

<sup>4</sup> Kooy. See Van 't Hoff, *Studien zur Chem. Dynamik*, 1896, 138.

<sup>5</sup> Reicher, *Lieb. Ann.* 232. 111.

<sup>6</sup> Ostwald, *Journ. f. Prakt. Chem.* [2] 27. 1.

<sup>7</sup> Hood, *Phil. Mag.* [5] 20.

<sup>8</sup> Schwab, Van 't Hoff, *Studien zur Chem. Dynamik*, 1896, 133, 134.

<sup>9</sup> Van 't Hoff, l. c. p. 132.

<sup>10</sup> Evans, *Zeitschr. f. Phys. Chem.* 7. 356.

<sup>11</sup> Sabatier, *Comptes Rendus*, 106. 63.

<sup>12</sup> Hecht and Conrad, *Zeitschr. f. Phys. Chem.* 3. 473.

<sup>13</sup> Goldschmidt and Reinders, *Berl. Ber.* 29. 1369.

<sup>14</sup> Spohr, *Zeitschr. f. Phys. Chem.* 2. 195.

<sup>15</sup> Buchbück, l. c. 23. 156.

<sup>16</sup> Clausen, *Landw. Jahrbücher*, 19. 894.

<sup>17</sup> Tammann, *Zeitschr. f. Phys. Chem.* 18. 433.

for measurements of velocity at temperatures easily reached ( $0^{\circ}$  to  $100^{\circ}$ ), neither proceeding too fast nor apparently not taking place at all.

Considering again the case of dibromsuccinic acid, with the fundamental equation

$$-\frac{dC}{dt} = kC,$$

and the integrated form of it

$$\log \frac{C_0}{C_t} = kt,$$

we get for the time required to half complete the reaction

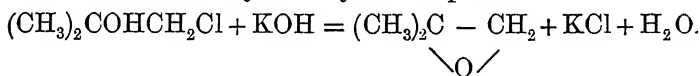
$$kt = \log 2 = 2.30256 \times 0.30103 = 0.693,$$

so that

$$t = \frac{0.693}{k} \text{ minutes,}$$

which gives at  $15^{\circ}$ , with  $k = 0.00000967$ ,  $t = 71690$  minutes, i. e. more than a month and half; whilst at  $101^{\circ}$ , with  $k = 0.0318$ ,  $t = 22$ , i. e. less than half an hour.

It must be added that the duration of polymolecular reactions may be prolonged at pleasure, so that it was possible to measure the very high velocity  $k_{43.6} = 1100$  of the action of dimethylchlorhydrin on potash:



Centinormal solutions were used for that purpose.

## 2. Influence of Temperature on Velocity from the Theoretical Point of View.

*Velocity in transformation cells and velocity of freezing.*

On p. 184 a case was described in which the velocity of reaction could be calculated from other quantities, viz. from the electromotive force ( $E$ ) of a transformation cell, and its conductivity ( $L$ ). The velocity ( $v$ ) of the transformation is proportional to these quantities, and so may be written

$$v = aEL \quad (1)$$



in which  $a$  is a constant depending on the units, and does not change with temperature, so that the influence of the latter on the velocity depends on the variations of  $E$  and  $L$ .  $E$ , according to p. 186, depends on the heat of transformation  $q$  in the following way:—

$$E = q \frac{P - T}{P},$$

where  $P$  is the absolute transformation temperature. In that way equation (1) may be changed, by introducing a new constant into

$$v = b (P - T) L,$$

in which  $L$ , the conductivity, has in general a value increasing with the temperature.

Above the transformation temperature, then, an increase is to be expected on two grounds, since  $P - T$  and  $L$  both increase. Below the reaction takes place in the reverse way, and while on fall of temperature the increase of  $P - T$  is a cause of acceleration, the change in  $L$  produces the opposite effect. So far as studied, the phenomena of transformation show corresponding changes in their velocity. Above the transformation temperature the velocity increases steadily; below it appears—e. g. in sulphur (transformation temperature  $95.6^\circ$ )—first to increase, reaches a maximum at about  $35^\circ$ , and then falls off, being extremely small at  $0^\circ$ . More exact measurements have been made on the corresponding phenomena of solidification by Gernez<sup>1</sup> for phosphorus and sulphur, and by Tammann<sup>2</sup> for benzophenone and some organic compounds. All these substances show a maximum velocity like that observed in the case of sulphur, and slightly below the freezing point the velocity is approximately proportional to the degree of undercooling.

*Influence of temperature on velocity in dilute homogeneous systems.* The so-far unknown law governing the influence of temperature on the velocity of reaction in

<sup>1</sup> *Journ. de Phys.* [2] 2. 159.

<sup>2</sup> *Zeitschr. f. Phys. Chem.* 23. 326.

homogeneous dilute systems, i. e. gases and solutions, must, as with the influence of the solvent (p. 221), include as a consequence that of temperature on equilibrium. Hence we have a starting point in the expression

$$\frac{dK}{dt} = \frac{d}{dT} \Sigma n \log C = \frac{q}{2T^2},$$

for the latter, which has already been explained. The influence of temperature may be divided *a priori* into two factors, in the same way as the influence of the solvent; the first, acting differently on the two reciprocal reactions which produce equilibrium, corresponds to the displacement of equilibrium; the other affects the two reciprocal reactions, and perhaps all reactions, alike. From the theoretical point of view it may be shown further that there is no displacement of equilibrium when

$$q = 0,$$

so that the temperature law may be expected to take the simplest form in reactions which are unaccompanied by any thermal effect. The mutual conversion of optical isomers such as right- and left-handed malic acid would be an ideal case.

In the absence of data of that kind it is of interest to discuss the functions of velocity and temperature which are in harmony with the above function of equilibrium and temperature. Let us, for that purpose, transform the latter expression so as to make it contain the velocities explicitly.

Choosing, as on p. 202, concentrations corresponding to the quantities occurring in the reaction, so that the concentration of the first system may be written  $C_I$ , that of the second  $C_{II}$ , we have

$$\frac{d}{dT} \Sigma n \log C = \frac{d}{dT} \log C_{II}^{n_{II}} - \frac{d}{dT} \log C_I^{n_I}$$

and

$$\frac{d}{dT} \log C_{II}^{n_{II}} - \frac{d}{dT} \log C_I^{n_I} = \frac{d}{dT} \log k_{II} - \frac{d}{dT} \log k_I,$$

in which  $k_I$  and  $k_{II}$  (see p. 203) are the velocity constants of the reciprocal reactions; hence

$$\frac{d}{dT} \log k_{II} - \frac{d}{dT} \log k_I = \frac{q}{2T^2}.$$

The relation between the constants of velocity and the temperature must be of such a form that the difference between the reciprocal quantities may have the above form.

A form such as that adopted by Warder<sup>1</sup>,

$$(a+k)(b-t) = c,$$

obviously does not satisfy this condition.

The simplest,

$$\frac{d \log k}{dT} = \frac{A}{T^2}, \quad (1)$$

was adopted by Arrhenius<sup>2</sup> on that account; Van 't Hoff<sup>3</sup> obtained favourable results with the more complicated form

$$\frac{d \log k}{dT} = \frac{A}{T^2} + B. \quad (2)$$

This includes Arrhenius' relation as a special case ( $B = 0$ ) and (with  $A = 0$ )—the oldest adopted—that of Berthelot<sup>4</sup>,

$$\frac{d \log k}{dT} = B. \quad (3)$$

Still other formulae have been proposed, which would have to be brought into agreement with a further development of the fundamental equation:

$$\frac{d \log k_I}{dT} - \frac{d \log k_{II}}{dT} = \frac{q}{2T^2}.$$

$q$  here is the heat developed by the reaction; it is not, as a rule, quite constant, but changes on account of the difference of the specific heats  $S_1$  and  $S_2$  of the two systems. Application of the law of Hess gives us the following:—

<sup>1</sup> Berl. Ber. 14. 1365.

<sup>2</sup> Zeitschr. f. Phys. Chem. 4. 226.

<sup>3</sup> Études de Dynamique Chimique. Amsterdam, 1884.

<sup>4</sup> Ann. de Chim. et de Phys. 1862, p. 110; Hood, Phil. Mag. [5] 20.

Passing from the second system to the first at  $T$  we gain  $q_T$ , then on fall of temperature to  $0^\circ$  we gain  $S_1 T$ ; if the second be then formed the gain of heat is  $-q_0$ , and finally, on rise of temperature to  $T$ , the gain is  $-S_2 T$ . According to Hess, then,

$$q_T + S_1 T - q_0 - S_2 T = 0,$$

or

$$q_T = q_0 + (S_2 - S_1) T.$$

Accordingly the above expression becomes

$$\frac{d \log k_{II}}{dT} - \frac{d \log k_I}{dT} = \frac{q_0 + \alpha T}{2T^2}.$$

If then we follow out Arrhenius' procedure we get

$$\frac{d \log k}{dT} = \frac{A + BT}{T^2}, \quad (4)$$

a form proposed by Kooy<sup>1</sup>, from which, as a special form ( $A = 0$ ), may be derived that of Harcourt and Esson<sup>2</sup>:

$$\frac{d \log k}{dT} = \frac{B}{T}. \quad (5)$$

All these forms are included in the expression

$$\frac{d \log k}{dT} = \frac{A}{T^2} + \frac{B}{T} + C. \quad (6)$$

It is so far impossible to choose between the above equations. Arrhenius introduces into his the idea that the increase of velocity rests on an increasing dissociation of the molecules, and that that follows the law of dissociation in its original form. In this case it might be expected that with increase of the number of molecules taking part in the reaction, an increased influence of temperature should be observed, because then the dissociation proceeding in a larger number of molecules would favour the velocity. This consequence does not follow from any equation, and the latter allows of the distinction of an influence  $\left(\frac{A}{T^2}\right)$

<sup>1</sup> *Zeitschr. f. Phys. Chem.* 12. 155.

<sup>2</sup> *Proc. Roy. Soc.* 58. 112.

acting unequally, and connected with the displacement of equilibrium, since for reciprocal reactions

$$\frac{A_1}{T^2} - \frac{A_2}{T^2} = \frac{q}{2T^2},$$

whilst the temperature effect, which is the same for both reactions, is expressed by  $B$ .

Another consideration yet may be drawn from the relation

$$\frac{d \log k_2}{dT} - \frac{d \log k_1}{dT} = \frac{q}{2T^2},$$

in reply to the question whether the ratio of velocities for  $10^\circ$  difference of temperature—say between  $0^\circ$  and  $10^\circ$ —can vary much from one reaction to another. This may be quite clearly decided in the case of reciprocal reactions like the formation and dissociation of hydrochloric acid. Integrating on the assumption that  $q$  is constant over the interval of  $10^\circ$ , we get

$$\log_e \frac{k_1}{k_2} = -\frac{q}{2T} + \text{const.}$$

and

$$\log_e \left( \frac{k_2}{k_1} \right)_{10} - \log_e \left( \frac{k_2}{k_1} \right)_0 = \frac{q}{2} \left( \frac{10}{273 \times 283} \right),$$

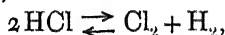
i. e.

$$\log_{10} \left\{ \left( \frac{k_2}{k_1} \right)_{10} \div \left( \frac{k_2}{k_1} \right)_0 \right\} = \frac{5q}{2.3 \times 273 \times 283} = \frac{q}{395.39}$$

or

$$\left( \frac{k_2}{k_1} \right)_{10} \div \left( \frac{k_2}{k_1} \right)_0 = 10^{\frac{q}{3953.9}}.$$

The greatest divergence will occur, therefore, for reciprocal reactions which are accompanied by a great evolution of heat. Taking one of the highest values, for formation of hydrochloric acid,



we have

$$q = 44000 \quad \text{and} \quad \left( \frac{k_2}{k_1} \right)_{10} \div \left( \frac{k_2}{k_1} \right)_0 = 17.2.$$

The most divergent temperature coefficients yet observed

(p. 228) are 7.14 for ferment action and 1.2 for arsine, i. e. in the ratio 6 : 1.

### 3. *Temperature of Inflammation.*

Let us now make use of the leading result on the connexion between velocity of reaction and temperature, viz. that equal ratios of velocity accompany equal differences of temperature. We come at once to the consequence that a reaction which takes place at any temperature must take place at any other temperature.

In sharp contradiction with this we have a series of instances, known long before any velocity of reaction was measured, in which no reaction at all takes place up to a certain limit of temperature; reaction sets in only at a certain temperature, which in the case of combustible substances is called the temperature of inflammation<sup>1</sup>. Attention has of late been drawn to similar phenomena, especially by Pictet, with the aid of modern cooling appliances. Almost all the reactions that proceed energetically at ordinary temperatures are practically stopped by these low temperatures. Sodium and hydrochloric acid do not act on one another visibly at  $-80^{\circ}$ . A more exact study, however, of just that case<sup>2</sup> shows that it is really a retardation; the hydrochloric acid, after having been—apparently without reaction—in contact with sodium, is found to contain sodium. The same has been observed of most phenomena of explosion, i. e. that a slow reaction takes place below the temperature of explosion, and that temperature accordingly does not mean a sudden setting in of a reaction which has no existence below it. In the case of reactions accompanied by evolution of heat, it is to be expected that the evolution of heat should produce an acceleration which may give an explosive character to the slow reaction already existing.

<sup>1</sup> L. Meyer, *Dynamik der Atome* (1883), p. 417; Bunsen, *Gasometrische Methoden* (1877), p. 336.

<sup>2</sup> Dorn and Völlmer, *Wied. Ann.* 60. 468.

These considerations, however, do not answer the question completely, and the new observations on 'apparent equilibrium' especially bring again into prominence the view that, by following the velocity of a reaction systematically downwards, a point will be reached at which it vanishes altogether. Indications of this are to be found already in the slow oxidation of phosphorus. That substance inflames at a temperature often stated at  $40^{\circ}$ , but as a matter of fact varying considerably with circumstances. Inflammation leads, with a large evolution of heat, to formation of phosphorus pentoxide; but it is preceded by a slow oxidation, accompanied by phosphorescence, and leading to formation of the oxide  $P_2O^1$ ; this slow oxidation seems, on fall of temperature, to end at a definite lower limit. Fig. 62 (p. 211) shows this plainly. It contains the result of measurements by Joubert which aimed essentially at determining the pressure limit, and shows that phosphorescence, and therefore oxidation, occurs only below 355 mm. at  $1.4^{\circ}$  and 760 mm. at  $19.2^{\circ}$ , whilst between those points the pressure limit is practically a linear function of the temperature. From this it immediately follows that for a given pressure there exists a limiting temperature below which the phosphorescence ceases entirely, e.g. at 529 mm. the limit is at  $8.9^{\circ}$ . It may be added that the explosion of a mixture of phosphine ( $PH_3$ ) and oxygen has also a pressure limit varying with the temperature, and the same conclusions may be expected to hold.

However the limit in question may depend on circumstances (e.g. moisture), still the connexion it shows with the recently observed phenomenon of 'apparent equilibrium' makes it a matter of the highest interest.

### C. Influence of Pressure on Velocity of Reaction.

The influence of pressure is that which seems to fall most easily into the domain of thermo-dynamic treatment, and

<sup>1</sup> Besson, *Comptes Rendus*, 124. 763.

so might well be dealt with before that of temperature, were it not that, on account of experimental difficulties, the question as to the influence of pressure on the velocity of reaction has only been answered in a few isolated cases.

A distinction of two kinds must be made here. In case of change of pressure in dilute gases (or change of osmotic pressure in dilute solutions) the effect on the velocity is given *a priori*, and is confirmed by experiment. We may, therefore, briefly refer to previous deductions and considerations. The pressure (in kilograms per sq. metre) in such cases is given by the equation

$$APV = 2T,$$

in which  $V$  is the volume (in cub. metres) containing one kilogram-molecule. With the unit of concentration adopted (gram-molecules per litre) we have

$$V = \frac{1}{C}$$

and accordingly

$$AP = 2CT.$$

If several gases are mixed, then

$$C = C_I + C_{II} + \dots = \Sigma C,$$

and the equation becomes

$$P = \frac{2T}{A} \Sigma C.$$

Since now one of the velocities is given by

$$-\frac{dC}{dt} = kC_I^{n_I} C_{II}^{n_{II}} \dots = kC^{\Sigma n},$$

velocity and pressure are connected in a known manner.

We may now more easily answer the question as to the influence of a change of pressure on the velocity. Since by the above the pressure is directly proportional to the concentration, it follows from the last equation that for the velocities under pressure  $p$  and  $P$

$$\left(-\frac{dC}{dt}\right)_p : \left(-\frac{dC}{dt}\right)_P = \left(\frac{p}{P}\right)^{\Sigma n} = \left(\frac{p}{P}\right)^N,$$



in which  $\Sigma n$  is the sum of the molecule ( $N$ ) taking part in the reaction. The ratio of velocities, however, refers to the change of concentration in unit time, i. e. to the amount transformed in unit volume. If we wish to know the whole amount transformed  $(-\frac{dS}{dt})$ , we must remember that

$$\frac{dS}{dt} = V \frac{dC}{dt},$$

so that

$$\begin{aligned} \left(-\frac{dS}{dt}\right)_p : \left(-\frac{dS}{dt}\right)_P &= V_p \left(-\frac{dC}{dt}\right)_p = V_P \left(-\frac{dC}{dt}\right)_P \\ &= \frac{P}{p} \left(\frac{p}{P}\right)^N = \left(\frac{p}{P}\right)^{N-1}. \end{aligned}$$

The total amount of reaction is thus independent of the pressure in monomolecular reactions, in which  $N = 1$ ; proportional to the pressure for bimolecular, i. e. for  $N = 2$ ; proportional to the square of the pressure for trimolecular, i. e. for  $N = 3$ .

We have already (p. 188) given the data which confirm this argument, only there it was not the pressure, but the accompanying change of volume or concentration, that was in question.

### 1. *Experimental Data.*

If for gases the problem is solved in its essentials, it is quite otherwise for the simple case of the effect of pressure on the velocity of reaction in liquids and solids; dilute solutions may here again be put first, since the laws of equilibrium are known for them. But the experimental data in this connexion are so scanty that they may be brought forward in full.

While Spring showed in numberless experiments that reactions, as e. g. combination of sulphur and zinc, may be brought about by the influence of pressure, and further, the occurrence of explosions due to pressure, such as of

dynamite, seems to prove that pressure may accelerate or occasion a velocity of reaction, the first measurements of change of velocity successfully carried out are those of Röntgen<sup>1</sup>. It was found that 500 atmospheres pressure reduces the rate of inversion of sugar by hydrochloric acid. Along with this ranks a more extensive research of Rothmund<sup>2</sup>, from which we quote the following:—

(a) A 20% sugar solution contains hydrochloric acid to normality. The velocity constant divided by 2.30256 (calculated with common logarithms) and multiplied by  $10^6$ , i.e.  $\frac{10^6 k}{2.30256}$  (time in minutes), was found:

Temperature.	Pressure.	$\frac{10^6 k}{2.30256}$	Temperature.	Pressure.	$\frac{10^6 k}{2.30256}$
16°	250 atms.	1664	15°	500 atms.	1337
16°	1 „	1702	15°	1 „	1416

i. e. a fall of 1% for 100 atmospheres, as Röntgen also found.

(b) A 5% methyl acetate solution with normal hydrochloric acid:

14°	500 atms.	1294	14°	200 atms.	1144
14°	400 „	1260	14°	100 „	1109
14°	300 „	1197	14°	1 „	1073

i. e. an increase in the velocity of reaction in this case, as was found also by Stern<sup>3</sup> to a greater extent for acetic acid and for ammonia:

0.2 gram-molecule methyl acetate + 0.175 gram-molecule acetic acid per litre.

Temperature.	Pressure.	$\frac{k}{2.30256}$ (time in minutes).
30.7° to 30.5°	500 atms.	0.0000194
30.7° to 30.5°	1 „	0.0000141
30.2° to 30.51°	500 „	0.0000203
30.2° to 30.51°	1 „	0.0000145

<sup>1</sup> Wied. Ann. 45. 98.

<sup>2</sup> Zeitschr. f. Phys. Chem. 20. 170.

<sup>3</sup> Wied. Ann. 59. 652.

## 2. Theoretical Discussion of the Influence of Pressure.

*Transformation cells.* Let us again take first for discussion the behaviour of a transformation cell (p. 182), in which the velocity of reactions depends in known manner on the electromotive force and the electrolytic conductivity. The influence of pressure on the velocity is then given by a knowledge of its influence on the above factors.

The effect produced by pressure on the electromotive force is known theoretically by a relation which has also been confirmed by experiment. If  $E_0$  is the electrical work, expressed in calories, which a reaction can perform, per kilogram-equivalent, without pressure, and if  $V$  is the increase of volume (in cub. metres) accompanying the reaction, then a pressure  $P$  (in kilograms per sq. metre) will absorb an amount of work expressed by  $APV$  in calories, and the electrical work will be reduced to

$$E_P = E_0 - APV,$$

and the electromotive force will be changed correspondingly. This equation, deduced by Gibbs<sup>1</sup>, has been experimentally confirmed by Braun<sup>2</sup> and Gilbault<sup>3</sup>, according to whom the Bunsen element, for example, at 100 atmospheres possesses an electromotive force lower by 4.05 millivolts against 3.83 calculated. This factor vanishes for reactions unaccompanied by change of volume, so that here too (p. 231) the mutual conversion of optical isomers would be the theoretically simplest case.

The influence of pressure on the conductivity is, since it has not yet been brought within the scope of theory, a quantity to be determined by experiment. For normal hydrochloric acid at 18°, a pressure of 260 atmospheres raises it 1.6 %; for normal acetic acid at 14°, 7.14 %<sup>4</sup>.

<sup>1</sup> *Thermodynamic Studies*, p. 396.

<sup>2</sup> *Zeitschr. f. Phys. Chem.* 1. 270.

<sup>3</sup> *Compt. Rend.* 113. 465.

<sup>4</sup> Fanjung, *Zeitschr. f. Phys. Chem.* 14. 685.

*Dilute solutions.* In considering the velocity of reaction in dilute solutions, we have again to place in the foreground the relation between velocity and equilibrium, and first to pay attention to the displacement of equilibrium by pressure. According to Planck<sup>1</sup>, this is given by the relation

$$\frac{d \log K}{dp} = \frac{\Delta v}{2T},$$

in which  $\Delta v$  is the change of volume (in cub. metres) when a kilogram-molecule of the first system is converted into the second ( $p$  in kilograms per sq. metre); there is therefore no displacement of equilibrium when there is no change of volume. The reaction constant stands in the relation already explained to the velocity constants:

$$K = \frac{k_{II}}{k_I},$$

so that

$$\frac{d \log k_{II}}{dp} - \frac{d \log k_I}{dp} = \frac{\Delta v}{2T} = \frac{V_{II} - V_I}{2T},$$

in which  $V_I$  is the volume of the first system,  $V_{II}$  of the second. Decomposition of this equation, as on p. 232, leads to the possible formula

$$\frac{d \log k}{dp} = \frac{V}{2T} + A,$$

which, if we neglect the change of volume ( $V$ ) produced by the pressure ( $p$ ), leads to

$$\frac{d \log k}{dp} = \text{const.},$$

i.e. equal ratios of velocity for equal differences of pressure, as is the case for temperature. The above data hardly suffice to test the conclusion.

<sup>1</sup> *Wied. Ann.* 32. 495; *Thermodynamik*, 1897, p. 218.

3. *Pressure of Inflammation.*

We have yet to arrive at the relation which necessarily exists between the effects of pressure and of temperature on reactions. As described on p. 210, there are indications of a discontinuous effect of temperature on velocity of reaction, and Fig. 62 (p. 211) gave for the phosphorescence of phosphorus the boundary between two regions as a function of pressure and temperature: in the lower, phosphorescence, i. e. oxidation, occurs; in the upper it does not. This boundary, which, according to some, separates the region of true from that of false equilibrium, must imply a discontinuity not only in the influence of temperature, but also in that of pressure. The course of the boundary is however peculiar, in that while rise of temperature causes oxidation to set in suddenly, fall of pressure is required for the same purpose. This is shown too by the striking discovery of Davy that phosphorescence first sets in below a definite pressure of oxygen. The fact is all the more important in that corresponding phenomena have been found in other cases. According to Joubert<sup>1</sup>, sulphur and arsenic behave like phosphorus; gaseous phosphine mixed with oxygen explodes on expansion<sup>2</sup>; silicon hydride behaves in the same way<sup>3</sup>, and the temperature of explosion of mixed oxygen and hydrogen falls from 620° to 540° on fall of pressure from 760 mm. to 360 mm.<sup>4</sup>; and aldehyde seems to be incapable of oxidation when the pressure of the oxygen is high<sup>5</sup>. The phenomenon in question has been followed out further for phosphine<sup>6</sup> ( $\text{PH}_3$ ), and it appears that even in the region of apparent equilibrium oxidation occurs, which, without any noticeable acceleration, leads,

<sup>1</sup> *Thèse*, 1874.

<sup>2</sup> Houton de Labillardière, *Ann. de Chem. et de Phys.* 16. 304; Van 't Hoff, *Studien zur Chemischen Dynamik*, 1896.

<sup>3</sup> Friedel and Ladenburg, *Ann. de Chim. et de Phys.* [4] 23. 430.

<sup>4</sup> Mitscherlich, *Berl. Ber.* 26. 399.

<sup>5</sup> Ewan, *Zeitschr. f. Phys. Chem.* 16. 340.

<sup>6</sup> Van de Stadt, l. c. 12. 322.

by a definite fall of pressure produced by the oxidation, eventually to explosion.

<i>Time in hours.</i>	<i>Pressure.</i>	<i>Fall of pressure per hour.</i>
0 . . . .	765	
2 . . . .	757	4
8 . . . .	737	3.3
12 . . . .	724	3.2
21 . . . .	696.5	3.0
25 . . . .	685.5	2.8
31 . . . .	665	3.4
34 . . . .	655	3.3

Explosion followed shortly afterwards.

#### D. Waves of Reaction.

So far we have been considering the velocity of a reaction which proceeds simultaneously and uniformly throughout the mass capable of reaction. Only in the discussion of contact action was there any mention of local effects, which, however, in that case remained localized. The phenomena now to be mentioned concern changes brought about by local causes in a substance or mixture capable of reaction, which then spread throughout the mass.

The possibility of such a propagation lies in the fact that the reaction may bring about changes which in turn are capable of causing or accelerating the reaction. Temperature and pressure are of the greatest importance in this matter, and a wave of high temperature or a wave of high pressure may be set up in a substance or mixture capable of reaction, which brings about complete or nearly complete conversion. The first of these is the long-known progressive combustion taking place, e.g., in gases, and studied by Bunsen among others; the second is the explosive wave, studied only in recent times by Berthelot and others.

##### 1. *Progressive Combustion.*

It is well known that certain bodies, as oxyhydrogen mixture, gunpowder, &c., may be totally transformed by local heating. The ultimate condition for that is that the

temperature required to initiate the reaction, 'the temperature of inflammation,' should lie below that which the reaction produces, or the 'temperature of combustion.' Let us therefore next state the essential points about these two temperatures.

(a) *Temperature of combustion.* In the first place, the temperature resulting from a reaction, in combustions called the 'temperature of combustion,' may be directly measured. Mallard and Le Chatelier<sup>1</sup>, e.g., found by means of the thermocouple<sup>2</sup> invented by the latter, that for a mixture of carbon monoxide and oxygen in the ratio  $2\text{CO}:\text{O}_2$  it is  $3200^\circ$ ; if instead of oxygen the equivalent amount of air be used it is  $2050^\circ$ . Theoretically we have to find the temperature to which the products of combustion are raised by the heat developed in the combustion<sup>3</sup>. If the evolution of heat is  $W$  calories and the specific heat constantly  $S$ , the rise of temperature  $\Delta$  is

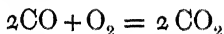
$$\Delta = \frac{W}{S}.$$

In the calculation attention must be paid to the difference—always small—between combustion at constant volume (e.g. in the calorimetric bomb) and at constant pressure (as in the usual process for measuring heats of combustion). The first is the case for explosions in a closed space, the second in the flame, and clearly, in the latter case, in consequence of free expansion an amount of heat is converted into work, which for each kilogram-molecule amounts to

$$APV = 2T$$

in calories, or at the usual temperature  $2(273 + 17) = 580$ .

The heat of combustion at constant pressure  $W_p$  has been found for carbon monoxide ( $\text{CO} = 28$ ) to be 68000. According to the equation



a decrease in volume occurs amounting to that of a

<sup>1</sup> *Comptes Rend.* 93. 1014.    <sup>2</sup> Holborn, *Physikalisch-technische Reichsanstalt*, 1896.

<sup>3</sup> Bunsen, *Gasometrische Methoden*, 1877, p. 308.

half kilogram-molecule per kilogram-molecule of carbon monoxide, and thus representing 290 calories. That amount is included in the 68000, so that at constant volume  $W_V$  for explosions in a closed space,  $68000 - 290 = 67710$  is to be taken as basis of calculation. Therefore in the former equation  $W$  has one of these values, provided that at the temperature reached by the combustion the carbon monoxide and oxygen unite completely, i. e. the carbon dioxide is not dissociated. Accordingly

$W_V = 67710$  (explosion of a carbon monoxide-oxygen mixture).

$W_P = 68000$  (flame of carbon monoxide in oxygen).

As to specific heat ( $S$ ) the matter is less simple. In the first place, the difference between the value at constant volume ( $S_V$ ) and that at constant pressure ( $S_P$ ) is much greater. The latter includes the work done in expansion under constant pressure  $P$ , i. e. in calories  $APdV$ , so that

$$S_P dT = S_V dT + APdV.$$

If we take the specific heats to refer to the kilogram-molecule we have

$$APV = 2T$$

and

$$APdV = 2dT;$$

hence

$$S_P = S_V + 2.$$

In the second place, we have to take account of the change in specific heat with temperature. Mallard and Le Chatelier<sup>1</sup> found for carbon dioxide at constant volume

$$S_V = 6.3 + 0.00564t - 0.00000108t^2.$$

Berthelot and Vieille<sup>2</sup> found, between 2000° and 4000°,

$$S_V = 19.1 + 0.0015(t - 2000) = 16.1 + 0.0015t.$$

<sup>1</sup> *Comptes Rend.* 93. 1014.

<sup>2</sup> *l. c.* 95. 1280; 96. 116, 1218, 1358, 1882; *Ann. de Chim. et de Phys.* [6] 4. 17.



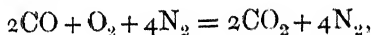
For nitrogen they found :

$$S_V = 5 + 0.00062 t,$$

and between  $2000^\circ$  and  $4000^\circ$  :

$$S_V = 6.7 + 0.0016 (t - 2000) = 3.5 + 0.0016 t.$$

Let us now calculate the temperature, observed as  $2050^\circ$ , obtained by burning a mixture of carbon monoxide and air according to the equation



where the air is expressed by the approximately correct formula  $\text{O}_2 + 4\text{N}_2$  and free expansion is allowed.

If the original temperature is  $0^\circ$  the heat required to raise the products of combustion of a kilogram-molecule of carbon monoxide to  $2000^\circ$  is, according to Mallard and Le Chatelier :

$$\begin{aligned} \int_0^{2000} (8.3 + 0.00564 t - 0.00000108 t^2) dt + 2 \int_0^{2000} (7 + 0.00062 t) dt \\ = 22.3 t + 0.00344 t^2 - 0.00000036 t^3 = 55480. \end{aligned}$$

There remain therefore  $68000 - 55480 = 12520$  calories for heating above  $2000^\circ$ . We may use the Berthelot-Vieille expression for the higher temperatures :

$$\begin{aligned} \int_{2000}^t (18.1 + 0.0015 t) dt + 2 \int_{2000}^t (5.5 + 0.0016 t) dt \\ = 29.1 t + 0.00235 t^2 - 67600. \end{aligned}$$

Thus the value of  $t$  has to be found from the equation

$$29.1 t + 0.00235 t^2 - 67600 = 12520$$

or

$$29.1 t + 0.00235 t^2 = 80120,$$

giving

$$t = 2322$$

as against  $2050^\circ$  observed. The difference is mainly to be attributed to uncertainty in the specific heats at high temperatures (Le Chatelier and Berthelot's formulae give for carbon monoxide and nitrogen at  $2000^\circ$  respectively 15.26 or 19.58 and 8.4 or 8.7), and to loss of heat during the combustion.

(b) *Temperature of inflammation.* Whilst the temperature of combustion can both be observed experimentally and calculated on theoretical grounds, there are uncertainties in both respects as to the temperature of inflammation.

Results of direct experiment appear to depend to a great extent on circumstances. Thus, e.g., Mallard and Le Chatelier<sup>1</sup> found for oxyhydrogen mixture  $500^{\circ}$  to  $600^{\circ}$  in closed vessels; Victor Meyer<sup>2</sup> confirmed this observation on the whole, but remarked that the slow oxidation already occurring at these temperatures may influence the result. Slowly streaming gas, led through a heated tube, did not take fire at  $650^{\circ}$  (temperature of boiling zinc bromide), but did at  $730^{\circ}$  (boiling zinc chloride)<sup>3</sup>. Hélier<sup>4</sup> recently stated that explosion does not occur below  $845^{\circ}$  on flowing through a porcelain tube; Mitscherlich<sup>5</sup> gave the temperature as constantly  $671^{\circ}$ , but added, in a later communication<sup>6</sup>, that using glass bulbs of varying dimensions it might vary from  $620^{\circ}$  to  $710^{\circ}$ .

In the method adopted it is hardly possible to avoid the influence of contact with the heating substance—glass surfaces, &c.—and that of the preceding slow combustion. Bunsen's<sup>7</sup> method is free from that uncertainty; it is based on the fact that in progressive combustion the temperature of combustion must be higher than the temperature of inflammation, and in the limiting case when the combustion no longer, or only just takes place, the two must be equal. The above measurements already give a certain confirmation of the law, since e.g. Meyer found for carbon monoxide a temperature of inflammation lying between  $650^{\circ}$  and  $730^{\circ}$ , i.e. far below the temperature of combustion. Bunsen then added oxygen to an explosive mixture of

<sup>1</sup> *Annales des Mines*, 4. 274.

<sup>2</sup> Krause and Meyer, *Lieb. Ann.* 264. 85.

<sup>3</sup> Freyer and Meyer, *Berl. Ber.* 25. 622; *Zeitschr. f. Phys. Chem.* 11. 28.

<sup>4</sup> *Berl. Ber.* 26. 162.

<sup>5</sup> l. c. p. 400.

<sup>6</sup> *Comptes Rend.* 122. 566.

<sup>7</sup> *Gasometrische Methoden*, 1877, p. 338.

oxygen and hydrogen to lower its temperature of combustion, and found that progressive combustion was possible in a mixture of one volume of oxyhydrogen gas to 9.35 of oxygen, but not with 10.47 of oxygen. Taking the mean, 9.91 oxygen to 1 of oxyhydrogen mixture, as the limit, we have to find the temperature of combustion of such a mixture. Bunsen calculated  $740^{\circ}$ , and that accordingly should be the temperature of inflammation.

There is uncertainty too as to the temperature of inflammation from the theoretical side. If it is true that there is a limit of pressure and temperature defining the region of apparent equilibrium (p. 210), explosion is simply the result of overstepping this limit. The latter must then be determined, only, if it exists, it undoubtedly depends much upon circumstances, since e.g. removal of moisture suffices to prevent many cases of combustion (p. 215). At the same time it is not necessary to assume the existence of such a limit in order to explain progressive combustion. In all the cases of combustion hitherto studied, the phenomenon is preceded by slow reaction below the temperature of inflammation. The heat wave propagated, e.g., in a gaseous mixture, after local heating, is on gradual rise of temperature accompanied by more and more of the reaction, until the heat so evolved in the wave makes up for the fall of temperature obviously attending the propagation, and leads eventually to a rise of temperature. The temperature of inflammation would thus be sharply defined as the limit at which the loss of heat which the wave suffers in its progress, by conduction, &c., is just balanced by the evolution of heat in the reaction taking place.

(c) *Wave velocity.* Besides the temperature of inflammation and of combustion the velocity with which the combustion is propagated is a characteristic factor. It was first measured by Bunsen<sup>1</sup>, and lately by Michelson<sup>2</sup>;

<sup>1</sup> *Gasometrische Methoden*, 1877, p. 317.

<sup>2</sup> *Zeitschr. f. Phys. Chem.* 3. 493.

the latter did so by allowing the gas to flow out with a velocity that just prevents the combustion from flowing backwards. This is easily attained by using a long glass tube, in which the flame can be seen to move to and fro according to the adjustment of the screw clip that regulates the velocity. If the flame is at rest the velocity of propagation ( $u$ ) in centimetres per second is given by

$$V = uS,$$

where  $V$  is the volume in cub. centimetres flowing out per second,  $S$  the cross-section in sq. centimetres. The following numbers were obtained,  $n$  being the volume per cent. of combustible gas:—

Carbon monoxide and oxygen.

$n = 25$	30	35	40	45	50	55	60	65	70	75	80	85	90	95
$u = 30$	40	49	58	66	73	80	84	88	91	91	85	70	45	20

Hydrogen and oxygen.

$n = 19.4$	21.8	83.8	86.9
$u = 121$	151	582	447

The maximum velocity does not therefore occur in the mixture which contains the gases in the proportion required for reaction. But it must be mentioned that Bunsen found very different values, e.g. 34 metres per second for oxyhydrogen mixture, as compared with 1.21 to 5.82 in the above experiments.

## 2. Explosive Waves.

A second phenomenon of propagation in mixtures or substances capable of reaction has only been made the subject of investigation in recent times. Although previously indications existed of a possible much greater velocity of propagation in explosives, it was first Berthelot and Vieille, and simultaneously Mallard and Le Chatelier, who followed out the phenomenon in question, and showed that besides the usual progressive combustion, which takes place in the oxyhydrogen mixture with a velocity of some metres per

second, a wave of reaction can occur in the same mixture, with a velocity a thousand times as great. Which of the two waves is set up depends essentially on the cause starting the reaction; by firing, i.e. by heat, the wave of combustion is set up; by a powerful local explosion (e.g. of fulminate of mercury), i.e. by pressure, the explosive wave.

The mechanism by which the propagation of an explosive wave is rendered possible has not yet been fully explained. It is, however, a fact that reactions can be set up by pressure or by a blow, and that they exert pressure. So that if the pressure developed exceeds that required to start the reaction, all the conditions for its propagation are satisfied. We will therefore consider in order these two pressures.

(a) *Pressure producing the explosion.* The rise of temperature produced in a gas by sudden change of pressure (or of volume) is calculable from the equation <sup>1</sup>

$$\frac{T}{T_1} = \left(\frac{v_1}{v}\right)^{k-1},$$

in which  $T_1$  and  $v_1$  are the original temperature and volume, e.g.  $273^\circ$  ( $0^\circ$  C.) and 1 atmosphere, whilst  $k$  stands for the ratio between the specific heats. Let us calculate what pressure ( $p$  in atmospheres) is needed to attain the temperature of inflammation  $T$ , on the assumption that the latter is not altered by pressure. Then  $k = 1.41$ , so that

$$\frac{T}{273} = p^{0.41}.$$

According to p. 247 the temperature of inflammation lies between  $650^\circ$  and  $730^\circ$ ; the corresponding pressures are 19.5 and 23.9 atmospheres.

(b) *Pressure produced by the explosion.* The pressure exerted in the reaction was first measured by Bunsen<sup>2</sup>, with the apparatus shown in Fig. 63. The vessel con-

<sup>1</sup> Clausius, *Mechanische Wärmetheorie*, 1887, p. 65.

<sup>2</sup> *Gasometrische Methoden*, 1877, p. 319; Mallard and Le Chatelier, *Compt. Rend.* 93. 1014.

taining the explosive mixture is closed above by a ground cover-plate pressed upon at *d* by a lever loaded at *b* and *a*. The fixed weight *a* serves to balance the longer arm of the lever, along the graduation of which the weight *b* is movable, in order to vary at pleasure the pressure closing the explosion chamber. *c* is a sheet of tinfoil, put into metallic connexion with mercury in the chamber by

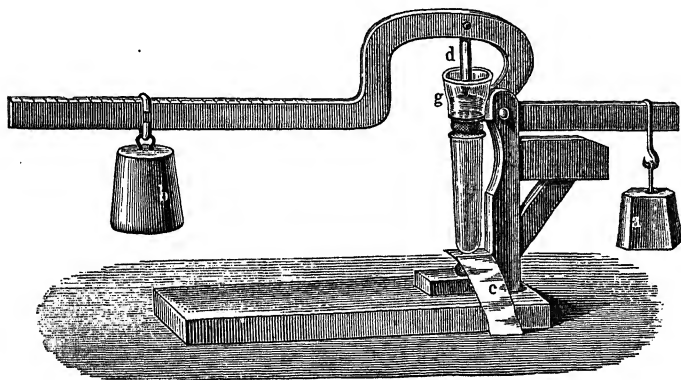


FIG. 63.

means of a platinum wire carried air-tight through the walls of the chamber. In order to make an inductive spark cross the whole length of the gas column, it is only necessary to connect one lead with the metallic lever-arm, and the other with the tinfoil. When the pressure caused by burning the gas is less than that exerted by the lever the gas burns without any noticeable explosion; in the opposite case the water placed for safety above the cover is thrown upwards with a noisy explosion. The limits of pressure at which, on the one hand, quiet combustion, and on the other explosion occur, may be drawn so close that the mean between them may be taken as the pressure sought:

Excess of pressure in atmospheres.

Carbon monoxide and oxygen 10·2, quiet combustion.

„ „ „ 10·04, forcible explosion.

Mean 10.12 atmospheres, excess of pressure: hence pressure of the mixture, 11.12 atmospheres<sup>1</sup>.

The production of pressure may also be followed numerically by finding the temperature caused by the explosion, as on p. 246. We are here concerned with the thermal value  $W_v$  of combustion of carbon monoxide at constant volume, which, according to p. 245, is per kilogram-molecule

$$W_v = 67710.$$

To heat the product of reaction, carbon dioxide, to 2000°, we require (using the specific heat at constant volume)

$$\int_0^{2000} (6.3 + 0.00564t - 0.00000108t^2) dt = 6.3t + 0.00282t^2 - 0.00000036t^3 = 21000.$$

For heating above 2000° there remain  $67710 - 21000 = 46710$  calories. These must equal

$$\int_{2000}^t (16.1 + 0.0015t) dt = 16.1t + 0.00075t^2 - 35200,$$

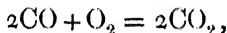
i. e.

$$16.1t + 0.00075t^2 = 35200 + 46710 = 81910,$$

whence

$$t = 4247.$$

If the original pressure is one atmosphere, the change in the number of molecules, from 3 to 2, according to the equation



would give, without rise of temperature, a pressure of  $\frac{2}{3}$  atmosphere; therefore with rise of temperature to 4247° C.

$$\frac{2}{3} \left( 1 + \frac{4247}{273} \right) = 11 \text{ atmospheres.}$$

Experiment and calculation agree in showing that the pressure produced does not suffice to generate the temperature of inflammation, since, according to p. 251, 20 to 24 atmospheres are needed. Still Mallard and Le Chatelier

<sup>1</sup> See also Berthelot, *Ann. de Chim. et de Phys.* [6] 4. 14.

showed, using a pressure indicator of Deprez, that temporary pressures much greater than 11 atmospheres occur, a phenomenon that may be explained on the assumption that combustion occurs in layers of gas already compressed. Dixon found, in confirmation, that glass tubes capable of standing a pressure of 25 atmospheres were shattered to fine powder by the explosive wave in a carbon monoxide-oxygen mixture, while they stood the ordinary wave of combustion. If the pressure arises from the explosion of layers already compressed, this would cause a gradually increasing local and transitory pressure, whose upper limit may be found by supposing that the layer in question is first brought to the 19.5 atmospheres required (p. 251) to produce the temperature of inflammation  $650^{\circ}$ , and that then explosion occurs, with rise of temperature of  $4247^{\circ}$ . The final pressure would then be

$$\frac{2}{3} \times 19.5 \left( 1 + \frac{4897}{273} \right) = 245.7 \text{ atmospheres.}$$

(c) *Velocity of explosive waves.* To measure the very high velocity of the explosive wave, a leaden tube, 40 metres long and at least 5 millimetres in internal diameter, was fixed zigzag on a wooden frame, and filled with the explosive mixture by means of inlet and outlet taps, which were then closed. At one end a little pastille of fulminate of mercury, weighing about a centigram, was placed and exploded electrically. The explosion travelling to the other end destroyed a strip of tinfoil, and so broke the electric current, and a chronometer of Le Boulangé measured the time between the making and breaking of the electric current. Some results may be given in connexion with the explanation that has been offered of the observed velocity.

Berthelot<sup>1</sup> brings the velocity ( $\theta$ ) of the explosive wave into relation with the velocity of translation of the mole-

<sup>1</sup> Berthelot, *Sur la Force des matières Explosives*, 1883, p. 118.

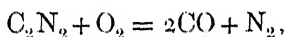


cules at the temperature of the explosion ( $T$ ). According to Clausius that is

$$\theta = 29.354 \sqrt{\frac{T}{d}},$$

where  $d$  is the density of the products of reaction, referred to air. Berthelot calculated  $T$  for this purpose from the heat of reaction and the specific heat of the products at constant pressure.

Dixon<sup>1</sup> sees in the explosive wave the analogue of a sound wave, whose velocity in the combustion, e.g., of cyanogen,



he calculates at 2310 metres per second.

Without going further into the two modes of calculation, we will put side by side their results and the observed velocities, calling special attention to the largest and smallest values; the numbers are for mixtures in equivalent quantities of oxygen and the gases named.

	<i>Berthelot.</i>		<i>Dixon.</i>	
	(Calc.)	(Obs.)	(Calc.)	(Obs.)
Hydrogen . . .	2810	2831	3416	2821
Acetylene . . .	2482	2660	—	2301
Ethylene . . .	2210	2517	—	2364
Cyanogen . . .	2195	2490	2310	2321
Ethane . . .	2363	2483	—	—
Methane . . .	2287	2427	—	2322
Carbon monoxide . .	1090	1940	—	—
Hydrogen and chlorine	—	1571	1830	1729

<sup>1</sup> Bakerian Lecture, *Phil. Trans.* 1893.

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